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SYNTHETIC FUELS FOR NAVAL APPLICATIONS PRODUCED USING SHIPBOARD NUCLEAR POWER

by
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Lieutenant, United States Navy

B.S., Mechanical Engineering
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Submitted to the Department of
Nuclear Engineering in Partial Fulfillment of the
Requirements for the Degrees of

NUCLEAR ENGINEER

and

MASTER OF SCIENCE IN NUCLEAR ENGINEERING

at the
Massachusetts Institute of Technology
June 1995

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ABSTRACT

This thesis evaluated the generation of synthetic fuels for the propulsion of naval aircraft and ships, on the premise that this could be a useful contribution to the logistical support of deployed naval forces. The feedstocks for the fuel are produced from the ubiquitous hydrogen and carbon dioxide available (with appropriate processing) in seawater. Previous work in this area, most of it one or two decades old, was reviewed, as were significant developments since. Various end product synthetic fuels were studied including hydrogen, methanol, and naval fuels (jet fuel and naval distillate) together with their respective applications. In addition the synthetic fuel is a recycled product, one that produces zero net carbon dioxide, thereby capable of - if adopted on a larger scale - mitigating the increase in atmospheric carbon dioxide concentrations now underway.

A large "nuclear fleet oiler" was identified as the preferable platform to provide sufficient fuel for a deployed carrier battle group. It generates 900 MW_e (3600 MW_{th}) from about three CVN size PWR nuclear reactor plants and employs a catalytic conversion chemical plant of proven technology to produce approximately 8200 barrels per day. This capacity amounts to about 55 % of the capacity of the terrestrial New Zealand natural gas-to-gasoline synthetic fuel plant, which is the premier present day commercial application of this technology.

Hydrogen generation by electrolysis proved to be the most energy intensive step in the overall process, consuming 80 % of the total required electric energy. Other potentially more efficient means for producing hydrogen were investigated and found to require a high temperature regime, one that could possibly be provided by a High Temperature Gas Cooled Reactor (HTGR). The process of extracting carbon dioxide from seawater was found to be a major area that needs further study since current methods (e.g. vacuum recompression distillation) are not specifically optimized for this purpose and methods proposed in earlier studies of this genre appear to be significantly flawed. While a synthetic fuel plant of this type may not be economically justified for commercial applications in the near term, the tactical and logistical freedom for a deployed naval force may warrant further, more detailed investigation.

Thesis Supervisor: Michael J. Driscoll
Title: Professor Emeritus of Nuclear Engineering

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I would like to extend my appreciation and gratitude to Professor Michael J. Driscoll, who not only introduced me to the subject of this thesis, but has spent much personal time and effort in advising me. His vast knowledge of all engineering disciplines and his practical engineering application skills provided great insight and motivation to this writer. Additionally, Professor A. Douglas Carmichael of the Ocean Engineering department, has continually provided enlightening discussions throughout this project. Furthermore, I would like to thank all the business and technical personnel contacted, for providing current information on the related commercial state of technology, all are mentioned or noted either as a reference or within the context of this thesis.

Most importantly, I would like to extend my sincere appreciation to my wife, Miriam, for without her support and unconditional love, this thesis and my entire educational experience at MIT could not have been possible.

All references and sources used for this thesis were unclassified and publicly available literature. Furthermore, although an active duty naval officer on duty under instruction, the author has worked independently of any government department or agency.

DEDICATION

This thesis is dedicated to my children, Danielle Ashley and Kevin Brian. It is only my hope and desire that during their lifetimes their generation will have safe, economical, and environmentally friendly forms of energy, and will not experience such energy crises as their parents observed during the "seventies". They are truly my light and joy of life, and it is to them that I dedicate this thesis.

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Chapter 1

INTRODUCTION

1.1 Foreword

The first maritime use of a pressurized water reactor (PWR) was forty years ago in 1955, aboard the USS Nautilus. Since that time, there have been over 760 PWRs installed and operated aboard marine vessels all over the world by many different countries (Appendix B). This considerably exceeds the approximately 375 land based Light Water Reactors (LWRs) operated world-wide, for generation of electric power during the same time period (N-1). Hence the use of nuclear power in the maritime industry, both militarily and commercially, has indeed, a well proven history.

A major advantage of powering marine vessels with nuclear power is the logistic independence it provides with respect to ship propulsion. The purpose of this thesis is to evaluate a shipboard nuclear power plant coupled with a synthetic fuel generation plant to extend the energy independence provided by nuclear power to other elements of a naval fleet, such as aircraft and support vessels. The shipboard plant could be aboard a nuclear powered aircraft carrier or on an auxiliary fuel ship with a nuclear power plant used primarily for generation of process energy. A synthetic fuel (material) is one which is produced by the combination of its components, which may themselves be compounds of smaller components (G-2). In the present case the synthetic fuel plant draws feedstock from the ubiquitous carbon dioxide present in the atmosphere or seawater and the hydrogen available through electrolysis of seawater. Although an aircraft carrier has energy independence for its own propulsion, it is dependent on aviation fuel to power the

aircraft embarked. The aircraft carrier synthetic fuel application would enable the ship to be totally energy independent and therefore provide maximum deployment capability. The alternative synthetic fuel plant on an auxiliary fuel ship also provides energy independence and improved logistical support by generating fuels in remote world locations for aircraft, ships, and land vehicle fueling. Both synthetic fuel plants can produce a hydrocarbon fuel without dependence on local oil reserves/refineries or long-range shipping. There are several other reasons for producing synthetic fuels; it is desirable to replenish dwindling traditional fuels, such as natural gas and petroleum, and to eliminate the pollutants and inert materials commonly associated with fossil fuels, thereby providing a clean-burning fuel as well as a fuel that is less expensive to handle and transport than the original raw material (P-2). Furthermore, there must always be an abundant, secure, and independent fuel supply for national defense. Finally, the proposed naval application can also serve as the prototype for subsequent commercial applications, which may become attractive in the next century if the carbon dioxide (CO_2) greenhouse effect is confirmed to be as deleterious as many now contend.

1.2 Background

1.2.1 Fossil Resources

While the immediate work is focused on naval applications, the motivation for this study, and the approach taken, must be understood in terms of the world's energy and environmental situation. Recently, the political, economic and environmental concerns of using the rapidly depleting fossil fuel inventory are once again making synthetic fuels a desirable alternative. Some conservative estimates suggest that

affordable-cost oil and natural gas resources will only last 50 more years while coal will last approximately 200 more years based on current consumption and production rates. This latter qualification is a crucial one, especially if developing countries fulfill their current plans for large increases in energy consumption.

References B-3, B-5, and M-1 provide more accurate data on and prognosis of the extent of the diminishing fossil fuel resources. To better understand the present day fossil fuel supply the terms "proved reserves" and "estimated resources" must be understood. Proved reserves are generally those identified resources which geological and engineering information indicate with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions (B-5). Estimated resources include the easily accessible proved reserves plus any resources for which geological evidence suggests their presence; however, in actuality they are either undiscovered or may not be economically recoverable. These resources are further subdivided into conventional resources which use currently accepted extraction techniques, and unconventional resources whose extraction techniques differ substantially. Oil from tar sands and shale are examples of unconventional resources. Estimated resources must therefore be provided at a progressively higher price to make recovery economical, which would at some point make unconventional sources competitive with conventional sources. Due to the many ambiguities in specifying the magnitude of resources and the need to confine the present review within tolerable bounds, proved reserves as reported in reference B-5 will be used.

The U.S. proved oil reserves ending in 1993 were 31 bbo. Based on the average 1993 U.S. production rate of a little more than 3 billion barrels of oil (bbo) per year (8.6 million barrels per day: about half of total U.S. consumption) and assuming a constant production rate, the U.S. proven oil resources would be depleted in approximately 10 years. Although a constant domestic production rate is overly simplistic, in actuality oil imports would increase significantly to offset the diminishing domestic resources. Similarly, on a worldwide basis, only 1009 bbo currently remains in proved reserves, of which the politically unstable Middle East controls 663 bbo. Therefore, assuming a constant world oil production rate of 23 bbo per year (as in 1993), amounts to roughly a 44 year constant rate oil supply based on today's proved reserves. As shown by the Persian Gulf war of 1991, the Middle East oil has and will continue to be a worldwide asset due to its relative low extraction costs and abundant supply. It can therefore be expected that the entire world will increase their dependence on Middle East oil making the Middle East a progressively more important region over the next half century.

The U.S. proved natural gas reserves ending in 1993 were 4.7 trillion m^3 (165 trillion ft^3) of proved reserves. Worldwide, the proved reserves were 142 trillion m^3 (5016.2 trillion ft^3). Converting into equivalent bbo (ebbo) shows 938 ebbo for worldwide and 31 ebbo for the U.S.. If a constant world natural gas production rate of about 14 ebbo per year (as in 1993) is assumed, it will amount to roughly a 65 year constant rate oil supply based on today's proved reserves. Similar to oil, the U.S. has already consumed over half its domestic supply of natural gas and has approximately 9 years remaining assuming a constant 1993 production rate.

Coal reserves are much more plentiful than either oil or natural gas, both on a worldwide and domestic basis. World coal proved reserves ending in 1993 were slightly more than 1 trillion tonnes (2.3 E15 lbs) which is equivalent to approximately 3,800 bbo. This exceeds the worldwide oil resources by more than a factor of 3. The U.S. has about 23 % of the world's coal (~ 860 equivalent bbo) which dwarfs our remaining 31 bbo of proved oil reserves. Obviously, the abundance of coal resources appears on the surface to be the solution to our energy problem; however, as will be shown later, coal like all other fossil fuels produces CO_2 which disputably causes an environmental problem. Table 1.1 summarizes the current U.S. and world proved reserves for oil, natural gas, and coal on an ebbo basis. Similarly, Table 1.2 summarizes the U.S. consumption and production rates for oil, natural gas, and coal.

The above discussion concerned all the major fossil fuels, however, it is solely petroleum or oil that is directly related to this work. Fuels for naval propulsion (excluding nuclear), similar to the transportation sector in general, have predominately been liquid petroleum based. Obviously, with the domestic reserves of petroleum declining, alternatives and solutions must be pursued. Petroleum has continuously supplied between 95% - 97 % of all transportation energy in the U.S. since 1958, and the transportation sector uses about 65% of all petroleum consumed (S-2). Due to such a large consumption rate of petroleum for transportation, it becomes obvious that the U.S. is no longer independent in transportation fuels. Although the large U.S. abundance of coal could be utilized to produce synthetic fuels, this option is not pursued for a naval option which requires high mobility and depends on ubiquitous feedstocks: while it is conceivable that

Table 1.1
U.S. and World Oil, Natural Gas, and Coal Proved Reserves (1993)
(taken from reference B-5)

	U.S. (ebbo)	World (ebbo)
Oil	31	1,009
Natural Gas	31	938
Coal	863	3,813

Table 1.2
U.S. Consumption and Production Rates for Oil, Natural Gas, and Coal (1993)
(taken from reference B-5)

	Oil	Natural Gas	Coal
Consumption* (ebbo/year)	6	3.8	3.6
Production* (ebbo/year)	3.1	3.5	3.8
Production/Consumption (%)	52	91	104
Reserves/Production (years)	10	9	227

* Rates assume 0 % growth rate

Navy ships could be coal fired (as they were many decades past), liquid fuel is essential for aircraft.

1.2.2 The Greenhouse Effect

Atmospheric CO_2 is largely transparent to solar radiation, however it absorbs an appreciable fraction of the outgoing infrared radiation from the earth. The equilibrium temperature at the earth's surface increases as more infrared radiation is absorbed, thus creating what is termed the "greenhouse effect" or global warming. Carbon dioxide is not the only greenhouse gas: others include; ozone (O_3), methane (CH_4), nitrous oxide (N_2O) and chlorofluorcarbons (CFC's). The expected contribution of these other greenhouse gases are individually less than that of CO_2, but collectively are about the same magnitude, (B-3). Of the 50% contribution of CO_2 to the greenhouse gases, approximately 35% are due directly from fossil fuel fired generation, while deforestation, agriculture, and industry are estimated to contribute 10%, 3%, and 2% respectively (H-5). Hence, the focus of CO_2 mitigation has usually centered on fossil fuel fired sources, primarily those in the transportation and electrical generating industries. Note also that our most abundant resource, coal, generates more CO_2 per unit energy than gas or oil, and that oil (or gas) from tar sand, shale or coal conversion is worse than direct use of coal in this regard. It is for this reason that the present analysis is restricted to non-fossil feedstocks.

Carbon dioxide has become the main focus of global warming for several reasons: it is the largest-impact greenhouse gas (~ 50 %), it is the best understood of all the greenhouse gases, and curtailing the emission rate of CO_2 is extremely difficult considering

the world's dependency on fossil fuels as an energy source. In 1992 the United Nations held the "Conference on Environment and Development," with participation by over 160 countries, which created a worldwide treaty on the framework for climate change. The U.S., on Earth Day in 1993 announced its "climate change action plan" to reduce emissions of greenhouse gases to the 1990 level by the year 2000 (B-9). Several other industrial nations enacted analogous plans, demonstrating the recent concern over global warming. Although the environmental concerns regarding CO_2 are well founded, reference I-1 reports that "Securing energy resources may become a more serious issue than the environmental problems after the year 2020 when we consider the possible shortages of oil and natural gas." Therefore, two fundamental problems arise from the present use of conventional fossil fuels. First, the supply of fossil fuels at acceptable production costs is finite and secondly, there exists significant concern that CO_2 as a combustion byproduct of fossil fuels creates a potentially detrimental environmental effect called global warming and unconventional fossil sources are even less desirable.

1.2.3 Naval-Applicable Precedent

With the above as background, we then turn to a more central concern of the present thesis, namely that secure fuel supplies must always be available and plentiful to support national defense. Paradoxically, with the federal government streamlining currently in progress, the Naval Petroleum Reserves, containing the largest oil fields in the country, have been earmarked for sale. Coupled with the demise of the synfuels programs of the 1970's, this leaves the U.S. increasingly short of energy independence in the area of transportation fuels. Virtually the only palliative measure now in effect is the

establishment of a 60 day petroleum inventory in the form of the Strategic Petroleum Reserve. Hence, the entire premise of this thesis is to generate a synthetic liquid fuel for naval purposes utilizing nuclear power plants for process energy. In the proposed system, no fossil fuels are consumed and no net CO_2 is emitted in the process, creating a totally recyclable and independent fuel supply. A further goal is to carry out this process as close to the point of consumption as possible, thereby improving naval task force logistics. In addition, significant emphasis has been place on accomplishing these goals using proven technology to the maximum extent practicable. Finally, this concept is also synergistic with current national needs and R & D initiatives, which would greatly facilitate its development and implementation.

This concept has been studied and reported on by others in the past. Reference S-5, written by a Chilean Naval Officer, and reference B-2, written by a U.S. Naval Officer, offer two comparable studies of nuclear generated synthetic fuels for naval uses based on technology existing in the early to mid 1970's. Since then additional studies have been made on closely related topics. References C-4 and C-5 are based on work performed at the Grumman Aerospace Corporation dealing with the manufacturing of gasoline and/or kerosene from CO_2 and H_2. Those studies were further applied to a synthetic fuel production ship powered by an onboard nuclear reactor (C-6). However, most of the present and past work in this area received its impetus from the program carried out at Brookhaven National Laboratory (BNL), specifically that by Meyer Steinberg. Steinberg should be considered the architect of the application of nuclear power with CO_2 and H_2, since his writings on that topic and related topics has spanned

three decades. Much of the BNL work was specifically applied to nuclear fusion reactors, although some utilized generic nuclear power (fission or fusion). References S-6 through S-12 are the predominant sources of information documenting this work.

In view of the above discussed political, economic, environmental, and technological changes that have taken place over the past twenty years it was considered appropriate to revisit the subject of nuclear-generated synthetic fuel for naval applications.

1.3 Outline

As just established, the objective of this thesis is to propose and analyze systems utilizing nuclear power plants as the main source of energy to produce a synthetic fuel, from non-fossil feedstocks, useful for naval aircraft or ships. In pursuit of this goal, Chapter 2 provides an overview of selected, relevant past and present synthetic fuel plants and related processes that have proven successful. Chapter 3 analyses the various fuels needed for naval uses with the associated engines used for propulsion and electric generation. It also discusses the mission requirements which define the synfuel plant capabilities. Chapter 4 explains the process steps required to obtain hydrogen and carbon dioxide feedstocks. Chapter 5 outlines a conceptual design for the integration of the synthetic fuel plant and the nuclear power plant for an aircraft carrier, a barge and an auxiliary fuel ship. Finally, Chapter 6 presents a summary of the results, and makes conclusions and recommendations based on the work performed.

Chapter 2

OVERVIEW OF CURRENT PERTINENT SYNTHETIC FUEL TECHNOLOGIES

2.1 Introduction

Synthetic fuels have a long and varied history. The first notable synthetic fuel production was carried out in 1792 by a Scottish engineer named Murdock who distilled coal and utilized the coal gas product. However, of more interest to this work are more recent synthetic fuel developments and technology. Obviously, the production of synthetic fuels has not occurred on a grandiose scale, however, this chapter will discuss many large and small size plants currently or recently in operation that use technology which could be exploited in the proposed naval synthetic fuel plant.

The terms direct and indirect liquefaction must first be defined with respect to synthetic fuels having a genesis from coal conversion. Direct liquefaction is the process whereby the coal is partially broken down by hydrogenation to the level of the liquid product. This is schematically shown by the block diagram of Figure 2.1 (P-2). Direct liquefaction is presently not commercially available (I-2). Since this process is only specific to coal, it will not be discussed further. Indirect liquefaction is the production of liquid fuels from coal after first breaking down the coal in a gasification step. This is schematically shown by the block diagram of Fig. 2.2 (P-2). Although this process was defined for coal as a feedstock, it has also been associated with all processes which yield liquid fuels from a synthesis gas or syngas. Predominately, syngas is composed of carbon monoxide (CO) and hydrogen (H_2), although other various component combinations can occur: $CO_2/CO/H_2$, or CO_2/H_2. Three major indirect liquefaction processes fully

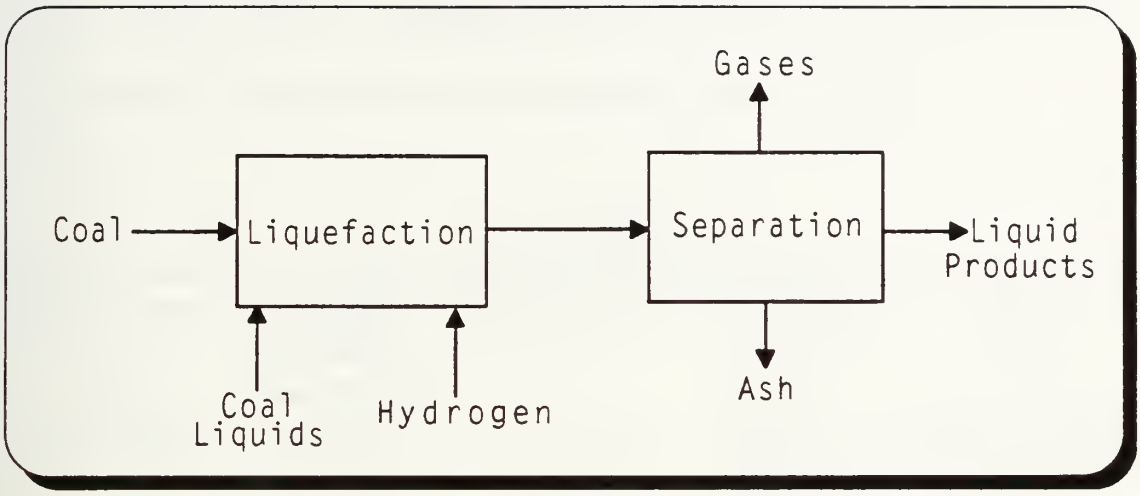


Figure 2.1
Direct Liquefaction of Coal.

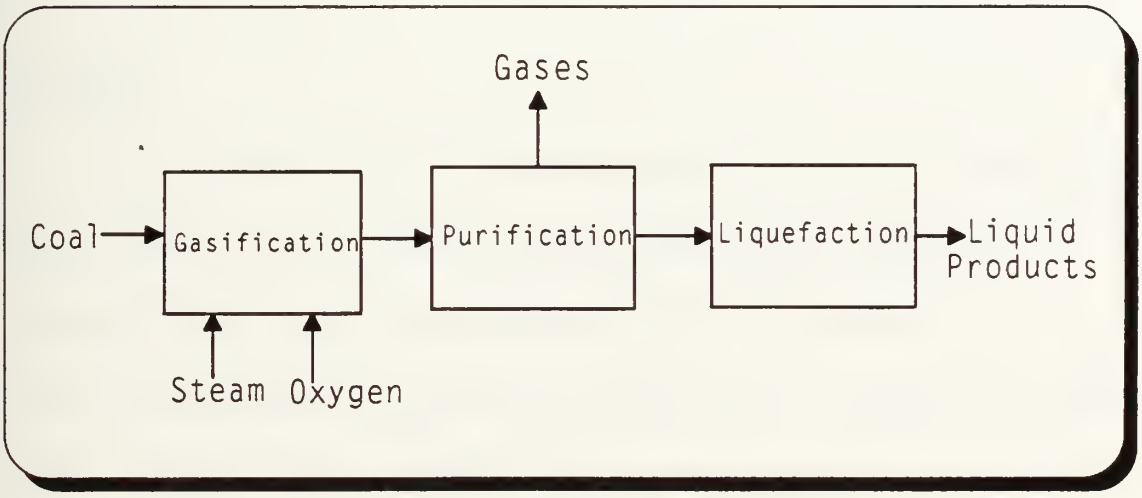


Figure 2.2
Indirect Liquefaction of Coal.

commercialized today are: methanol synthesis, Fisher-Tropsch, and Mobil methanol to gasoline (MTG). Table 2.1 summarizes the synthetic fuel plants or processes to be studied in this chapter with their applicable synthesis technology and end products.

Table 2.1
Relevant Synthetic Fuel Plants/Processes

Plant/Process	Synthesis Technology	Feed Stock	End Product	Catalyst
SASOL	Fisher-Tropsch	Coal	Gasoline	Iron Oxide
New Zealand	Methanol Mobil MTG	Natural Gas Methanol	Methanol Gasoline	Copper/Zinc Oxide Zeolite
Lurgi	Methanol	CO_2 and H_2,	Methanol	Copper/Zinc Oxide
Bruce	Methanol	CO_2 and H_2,	MTBE	*
Perry	Methanol	CO_2 and H_2,	Methanol	*

* Conventional methanol synthesis catalyst of copper/zinc oxide is assumed

2.2 SASOL

The South African Coal, Oil, and Gas Corporation, which is 30 % owned by the South African government, have been the world leaders of indirect liquefaction by operating the SASOL synthetic fuel plants based on Fisher-Tropsch synthesis. The Fisher-Tropsch synthesis is well known and is based on the work of Fisher and Tropsch of Germany during the 1920's. South Africa has a vast amount of coal reserves, and with SASOL they have substantially increased their energy independence. SASOL I began operation in 1955 and produces 1.25 E6 L/day (7800 barrels/day) of transport fuels and 1.7 E6 m^3/day (6.0 E7 ft^3/day) of medium caloric value gas from coal. In spite of the technical and economic problems experienced at this plant, the government remained

committed to the project (S-2). Subsequent to the oil crises of the 1970's, the government implemented a plan to construct two much larger plants, somewhat similar in design to SASOL I. SASOL II and SASOL III reached full production in 1982 and 1985 respectively. Both are identically sized with a capacity of 8 E6 L/day (50,000 barrels/day) of transport fuels, which is the predominant product (P-1). Unsubstantiated claims were made that suggested SASOL II and III produced gasoline that cost a little over $1 per gallon during the 1980's (S-2), making it very competitive with petroleum produced gasoline. Although the SASOL plants all use Fisher-Tropsch synthesis, which is not considered a serious option for today and future plants (S-2), they are noted here to show the diversity and experience gained with 40 years of operations.

2.3 New Zealand Methanol to Gasoline Plant

The New Zealand synthetic fuel plant was built as a result of measures taken by the New Zealand government to provide for security in their transport fuel supply following the oil shocks of 1973 and 1979 (M-2). New Zealand was fortunate to have two large natural gas fields available. The on-shore Kapuni field had estimated recoverable gas reserves of 419 petajoules (PJ) or 4×10^{14} Btu's while the off-shore Maui field had estimated recoverable gas reserves of 5193 PJ (5×10^{15} Btu's). A synthetic gasoline project was recommended to the government by the Liquid Fuels Trust Board (LFTB) for the utilization of these natural gas fields and to greatly increase New Zealand's self-sufficiency in transport fuels by the middle 1980's. The LFTB concluded, based on exhaustive comparative studies, that gasoline from natural gas via methanol provided the most economical and efficient method of producing synthetic fuel. The process developed

by the Mobil Oil Corporation was chosen and found to be better than the well known Fisher-Tropsch synthesis.

References C-2, C-3, and M-2 offer excellent descriptions of the New Zealand plant. The key to the Mobil process lies in a unique zeolite catalyst called ZSM-5, which possesses excellent shape selectivity due to its very regular three dimensional pure structure. Mobil's research during the early 1970's led them to this catalyst, which is composed of silica and alumina. The ZSM-5 catalyst extracts the water from the methanol and rearranges the hydrocarbons to leave gasoline which is essentially indistinguishable from crude oil produced gasoline. This remarkable reaction, whose detailed mechanism is yet unresolved, can be represented by the following overall reaction (C-2):

$$\frac{n}{2}(2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O) \rightarrow (CH_2)_n + nH_2O \qquad (2\text{-}1)$$

This equation first indicates an equilibrium of methanol with dimethyl ether (CH_3OCH_3) and water, followed by a mixture of (CH_2) products composed of olefins, aromatics and parafins.

The synfuel plant is located in Motonui, Taranaki and was designed to convert 4 million m^3 (140 million standard ft^3) per day of natural gas into 570,000 tonnes per year (14,500 barrels per day) of gasoline. This plant has two separate stages; the first stage converts the natural gas to methanol and the second stage converts the methanol to gasoline. Methanol yield is a strong function of the feed gas hydrogen to carbon (H/C) ratio. Natural gas from the Maui field is lean in carbon dioxide (7 %), so to increase the yield, feed gas from the carbon dioxide rich (44 %) Kapuni field is added (C-3).

The gas to methanol plant utilizes the Imperial Chemical Industries (ICI) low-pressure methanol synthesis process and has two methanol trains rated at 2200 tons per day. This phase desulphurizes the natural gas, combines it with medium pressure steam and passes the mixture through reformer reactor tubes containing nickel catalyst at 900°C to produce synthesis gas. The synthesis gas is cooled to 35°C and compressed to 10.3 MPa (1500 psia), where it is reheated and converted at 250-300°C over the ICI Cu-Zn catalyst to crude methanol and 17 % water (C-3). This stream is then fed to the methanol to gasoline (MTG) fixed bed reactor section containing the ZSM-5 catalyst. Shown in Fig. 2.3 is the MTG portion of the plant, which can be considered similar to the design required for a naval synthetic plant.

The New Zealand synthetic fuel plant has apparently performed quite well. The overall thermal efficiency (presumably the heat of combustion of the product divided by that of the input) of this gas to gasoline (GTG) plant is 54 % (M-2). With the addition of this synthetic fuel plant, New Zealand was able to achieve 50 % self sufficiency in liquid fuels in 1987, the first year of full operation. However, reference C-3 reports that at the (then current) price of $20/barrel for crude oil, the MTG was not competitive with petroleum for gasoline production. Nevertheless, since synthesis gas can be produced from any gasifiable carbonaceous material, such processes as the MTG may assume increasing importance as sources of oil and natural gas are depleted in the future. In March of 1993, Mobil relinquished its 25 % share of the synfuel plant, which is now owned solely by the International Methanex Corporation, the largest methanol manufacturer in the world.

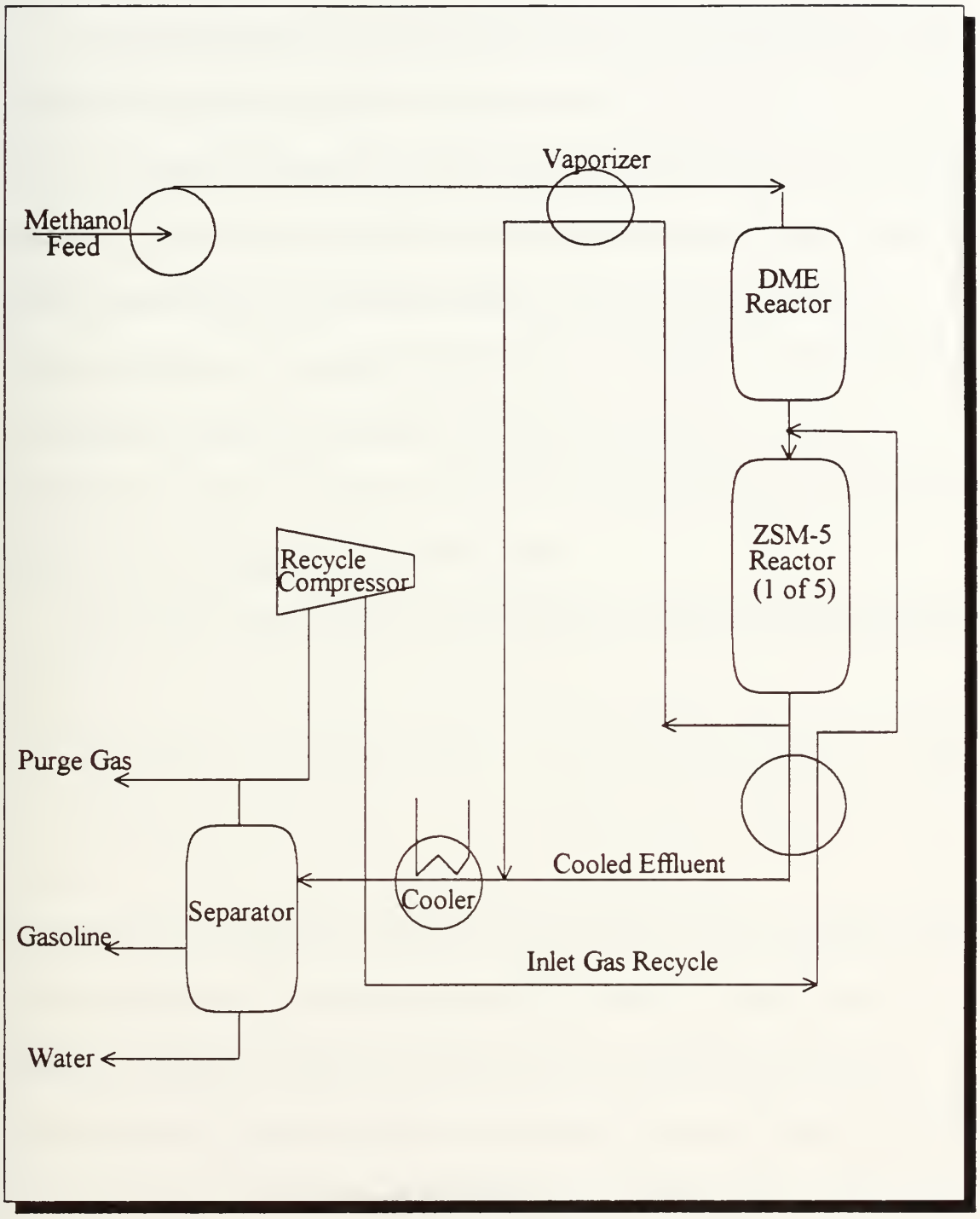


Figure 2.3
Mobil MTG Adiabatic Fixed Bed Process
(taken from reference M-6)

2.4 Lurgi Methanol Plant

Lurgi Oel-Gas-Chemie (Lurgi) of Frankfurt Germany recently announced a newly developed Cu/ZnO methanol catalyst for the conversion of CO_2 and H_2 into CH_3OH (H-2 and R-1). They have conducted pilot plant studies yielding excellent results and are now preparing to market a low to medium size methanol production plant. Lurgi, a worldwide chemical plant company, has a particular specialty in the design, engineering and construction of high and low pressure methanol plants. Previously, Lurgi has engineered and successfully marketed methanol plants utilizing feedstocks such as natural gas, naphtha, heavy residual oil and coal. It is from this vast experience base that Lurgi is now ready to produce methanol from CO_2 and H_2 solely.

The catalyst selected produces the following two parallel and equilibrium reactions (K-1):

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H = -49.43 kJ/gmole \qquad (2\text{-}2)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H = +41.12 kJ/gmole \qquad (2\text{-}3)$$

Methanol formation is reported to be favored by high pressure and low temperature, while high temperatures mostly favor the production of CO. Therefore, it seems logical to desire a low temperature catalyst (~ 200°C), however this temperature foregoes the economic benefit of cogenerating high pressure steam by operating at higher temperatures. Lurgi found that by increasing the catalyst temperature to between 260°C - 270°C they were able to achieve sufficient high pressure steam with good catalytic conversion and selectivity. Most catalysts used in Lurgi's other conventional methanol plants are also composed of Cu/ZnO. However, these catalysts will not perform well in a high CO_2

concentration environment. Therefore, in cooperation with Sud-Chemie, Lurgi developed this special variety of Cu/ZnO, designated a proprietary number of C 79-05-GL. The catalyst C 79-05-GL is expected to have a service life similar to other commercial catalysts of approximately four years.

Pilot plant tests have been very successful. Fig. 2.4 shows a simplified schematic of Lurgi's synthetic methanol plant configuration. The CO_2/H_2 methanol plant is reported to be 80 % the size and consume 20 % less energy when compared to other conventional Lurgi methanol plants (K-1). Designers think this new process can realistically compete for small to medium sized methanol plants, where they can exploit logistical advantages and where carbon dioxide and hydrogen are available feedstocks (H-2).

2.5 Bruce Energy Centre

The Bruce Energy Centre of Ontario Hydro and the Integrated Energy Development Corporation are currently in the process of developing a full-scale commercial model for sustainable development. Of interest to this thesis is the plan for the utilization of the Bruce Nuclear Generating Station "A" to produce methanol from carbon dioxide and hydrogen. Bruce Nuclear Generating Station "A" consists of four 769 MW_e CANDU reactors located in Tiverton, Ontario, Canada. Beginning construction in 1995, first planned is a 100 MW_e electrolytic hydrogen facility to be powered by off-peak, surplus or standby electricity. The carbon dioxide will be supplied from the Centre's fermentation ethanol plant and from the stack of Bruce's natural gas electric plant. The product methanol will be reformulated into methyl tertiary butyl ether (MTBE) for use as

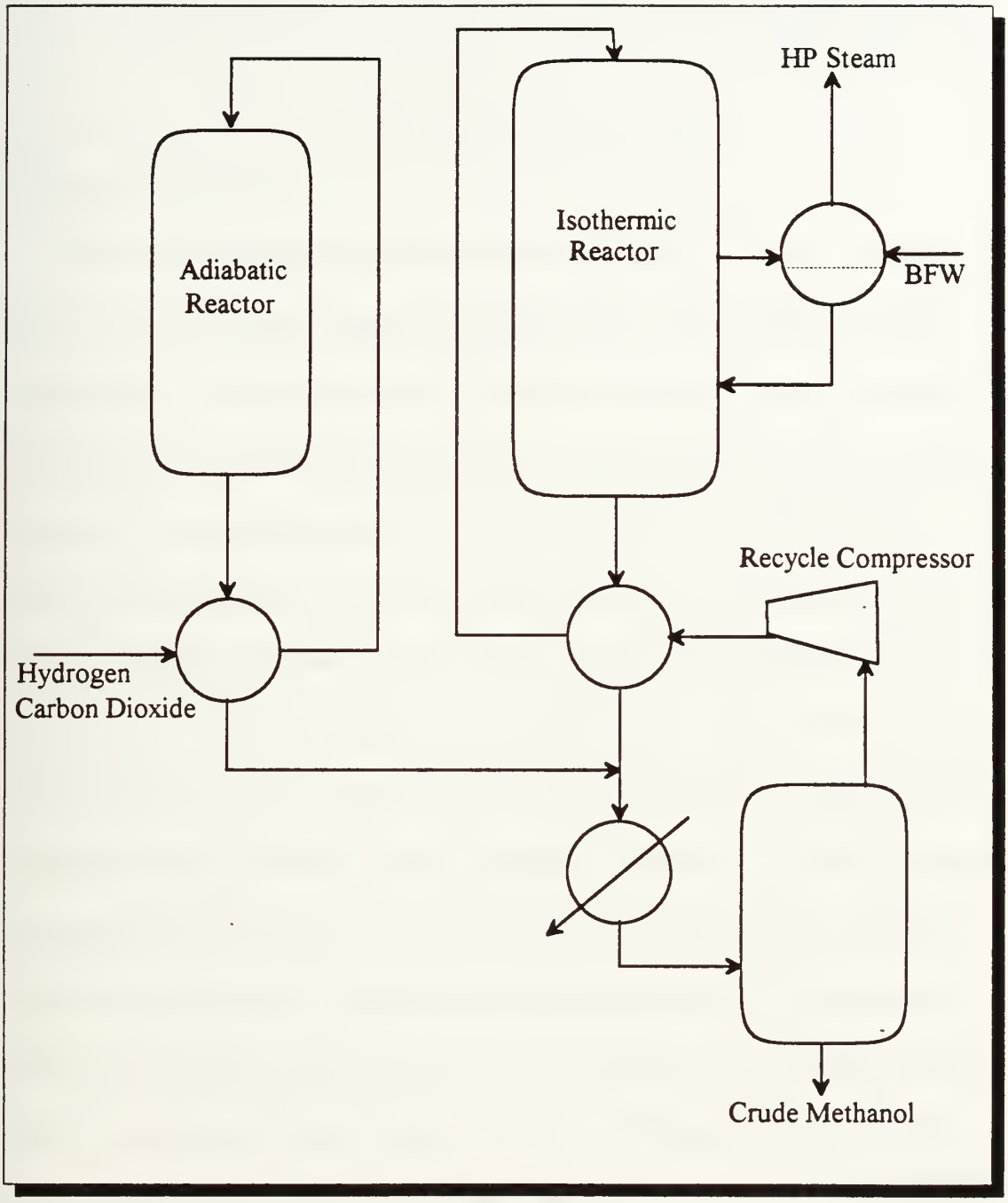


Figure 2.4
Simplified Schematic of Lurgi's Methanol Plant
(taken from reference K-1)

an additive to transportation fuels. The Bruce sustainable development model requires entrepreneurial innovation and no significant technological barriers need to be overcome; however, there have been no compelling political initiatives (G-1).

2.6 Perry Energy Systems

Perry Energy Systems of the United States developed and constructed in the early 1990's, a small demonstration methanol production plant utilizing carbon dioxide and hydrogen (M-3). The plant, named SSP-1A (Seafuel Synthesis Process, first variant), was to be located on a remote island in the Bahamas. The entire plant fit in a 8.5 m (28 foot) long van or cargo container, except for auxiliary supports like the diesel generator, sea and potable fresh water pumps. Fifteen solar panels provided power for lighting and charging the backup battery. Hydrogen was produced by an alkaline water electrolyzer process at a rate of 2 m^3/hr (71 ft^3/hr) at a pressure of 0.3 MPa (43.5 psi). Unique to this system was the source of CO_2. It was supplied by a bank of six compressed CO_2 cylinders which were replaced with fresh tanks when inventory diminished. Although not provided information, it is expected that the synthesis of CO_2 and H_2 to methanol used a typical commercial methanol synthesis catalyst of copper and zinc oxide in the reactor. The raw methanol produced was distilled to remove water and other impurities prior to storage as a usable product. A simplified schematic is shown in Fig. 2.5. Although never commercially successful, this unique plant provides another precedent for the type of application of current interest.

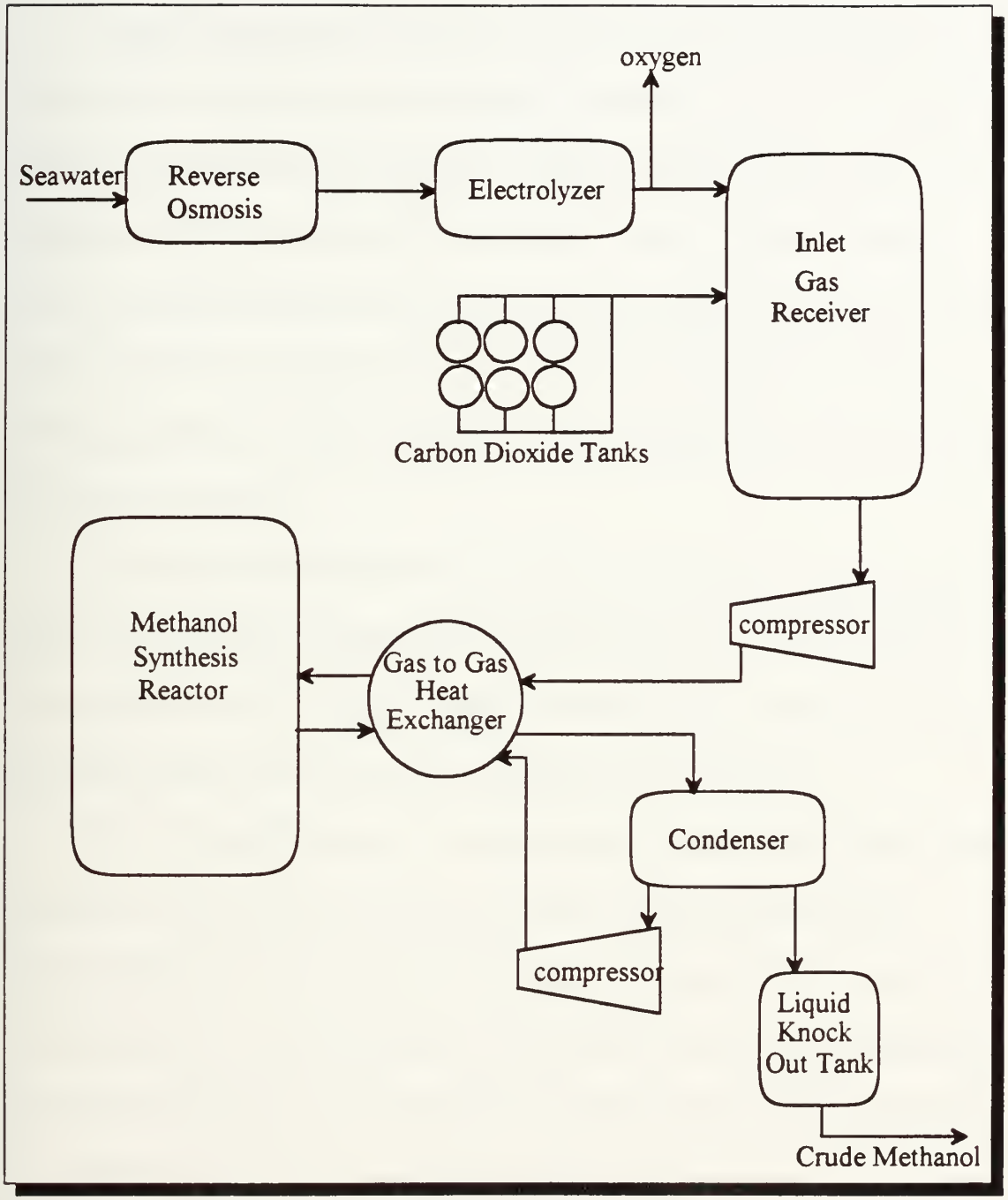


Figure 2.5
Simplified Schematic of Perry Seafuel Synthesis Process
(taken from reference M-3 and P-6)

2.7 Other Related Technologies

Toshiba is developing a low pressure catalytic conversion process to make methanol (S-13). Carbon dioxide and hydrogen are combined in a copper/zinc oxide catalyst operating between 200°C and 400°C. Unique to Toshiba's process is that hydrogenation of CO_2 is achieved at a pressure below 1 MPa (145 lb/in^2), whereas previous commercial methanol reactors operate at high pressures: between 10 to 15 MPa (1450 to 2175 lb/in^2). The size is therefore much smaller; correspondingly Toshiba is exploring using this low pressure operation as a direct installation in exhaust stacks of fossil fueled power plants.

It is clear that the least developed process step of this synthetic fuel concept is the retrieval of CO_2. Chapter 4 discusses in more detail specific means of capturing CO_2 and the various sources of CO_2 available. However, the following is an example of current industry R&D efforts to show the state of technology for CO_2 capture.

The Yokosuka CO_2 Removal Technology Laboratory of the Tokyo Electric Power Company is conducting pilot scale research on chemical absorption and physical adsorption methods to extract CO_2 from boiler exhaust gas stacks (O-5). The chemical absorption method, being developed jointly with Hitachi Ltd., uses a monoethanolamine as the chemical absorbing solvent. When heated, the absorbed CO_2 is released and collected or contained separately. The absorption unit operates at atmospheric pressure and at a temperature of 40 to 60 °C, while the regeneration portion operates at 0.1 MPa to 0.18 MPa (1.0 to 1.8 atm) and a temperature of 100 to 120 °C. The physical adsorption method, being developed jointly with Mitsubishi Heavy Industries, uses zeolite to

effectively adsorb CO_2. Flue gas passes through a zeolite bed at a temperature of 50 to 60 °C and pressure of 0.11 to 0.12 MPa (1.1 to 1.2 atm) where the CO_2 is preferentially adsorbed. The zeolite is later heated to 70 to 80 °C at a reduced pressure of 0.03 to .05 MPa (0.3 to 0.5 atm) in the desorption phase to remove the CO_2. Both methods have demonstrated results as high as 90% elimination rate with 99% purity.

2.8 Summary

This chapter briefly discussed five synthetic fuel plants that have significant relevance to this work in one way or another. The SASOL and Methanex plants both have a well proven history and technological base as well as being supported by their respective governments. The Lurgi and Perry plants are pilot or demonstration in nature, however, the Lurgi concept is presently set for commercialization. The Bruce methanol plant is one of many of Ontario Hydro's ongoing projects that shows their commitment to sustainable development. It is clear that over the past twenty years significant developments both in R&D and in commercial operation have taken place which demonstrate the feasibility of most of the process steps which will have to be configured to meet current objectives.

Chapter 3

NAVAL APPLICATIONS

3.1 Introduction

This chapter focuses on the present and future fuels; and prime movers that could be produced and utilized with a naval synthetic fuel plant. A naval fuel, whether for aircraft or ship propulsion, must have a moderate to high energy density, be clean burning, and offer safe storage and handling in a sea environment. The naval prime mover, similarly, must offer; high reliability, compactness, modest efficiency, and be easily operated and maintained at sea. Furthermore, the combination of naval fuel and prime mover must be the most reliable system possible, since they must propel ships or aircraft into, and possibly through "harms way" at any moment.

3.2 Fuel Selection

Reference M-4, completed in 1980, was an in-depth study conducted by the Maritime Transportation Research Board (MTRB) that reviewed potential (alternative) fuels that could become available to the maritime industry between the years 1980 to 2000. It also defined the economic, technical, environmental, and social impacts of alternate fuels on marine power plants. Although that study is now dated and was not specifically naval oriented, it does encompass similar objectives and constraints to the present investigation, mainly sustaining power at sea with alternative fuels on a marine vessel. Table 3.1 shows the various alternative fuels researched with the appropriate time frame that such fuel could be expected to become commercially available. The fuels bolded (methanol and hydrogen) are specifically of interest to this work. The others can

Table 3.1
MTRB Alternative Fuel Candidates
(abstracted from reference S-4)

Candidate Alternative Fuel	Commercialization Time Frame
1. Synthetic fuel from coal	1990's
2. Synthetic fuel from shale	1980's
3. Synthetic fuel from tar sands	1980's
4. **Methanol**	1990's
5. Methanol/Coal slurries	2000+
6. Ethanol	1980's
7. Gasoline/Alcohol blends	1980's
8. Pulverized coal/oil slurries	1980's
9. **Hydrogen**	2000+
10. Ammonia	2000+
11. Hydrazine	2000+
12. Methane	2000+
13. Nuclear	1980's
14. Coal	1980's
15. Wood	1980's
16. Solar energy	2000+
17. Wave energy	2000+
18. Wind energy	2000+
19. Ocean Thermal	2000+
20. Ocean Current	2000+

be discarded mainly due to our requirement of producing a synthetic fuel on board a ship with a nuclear reactor(s), be it an aircraft carrier or auxiliary ship. The MTRB study was also predominately directed toward land based production of synthetic fuels.

In addition to the MTRB study, a limited survey was conducted to examine all other possible and present alternative fuels. Many fuels were considered; however, two alternative fuels which are commonly overlooked are acetylene (C_2H_2) and ammonia (NH_3). The use of acetylene was suggested by reference B-11 as an alternative fuel for the internal combustion engine. It was proposed to use limestone (actually CaO) and coal to make CaC_2 which produced C_2H_2 by the following reaction.

$$CaC_2 + 2H_2O \Rightarrow C_2H_2 + Ca(OH)_2 \qquad (3\text{-}1)$$

Acetylene was shown to combust equally well in internal combustion engines as conventional fuels. However, coal and limestone, which are conventionally terrestrially mined, are required and therefore acetylene produced in this manner is not a suitable alternative naval fuel. Ammonia, proposed by reference S-9, is unlike most other alternative fuels since it can be produced by ubiquitous nitrogen (from air) and hydrogen (from sea water) by the following reaction.

$$3H_2 + N_2 \Rightarrow 2NH_3 \qquad (3\text{-}2)$$

Although this process may have great promise in a land based fuel application, or possibly as a fertilizer source, it is not useful in a naval application. Ammonia is extremely toxic,

there is little experience with it as a fuel, and it has a heating value (lower) of approximately 25,500 kJ/kg (~11,000 Btu/lb).

Thus, alternative fuels require mineral resources and for a naval application the mineral resources must be readily available, be easily produced, and have as little space requirements on the ship as possible. Since the present application only uses ubiquitous hydrogen and carbon dioxide, these mineral resources do not require remote supply or long term storage. Fuels briefly described below are the present naval fuels JP-5 and Diesel Fuel Marine (DFM), and prospective future naval fuels: methanol and hydrogen. Figure 3.1 shows the various pathways for alternative naval fuels. As seen, methanol should be considered a possible mid-term fuel while hydrogen is considered a potential long-term fuel. JP-5 or DFM can be synthesized given the present state of technology. Moving from the right to the left on Fig. 3.1 (i.e. moving into the future) reduces the energy and equipment requirements of the synthetic fuel plant; and thus increases the overall process efficiency.

3.2.1 JP-5

JP-5 is the predominant aviation fuel used by the U.S. Navy. It can also be used interchangeably with DFM as a substitute ship propulsion fuel (N-3). Unfortunately, DFM can not be used in gas turbines for aircraft use (H-4). However, caution should be taken when JP-5 is substituted for DFM since it has a tendency to loosen scale deposits from tanks and piping and could accumulate excessive particulate matter in the fuel system strainers. The MILSPEC for JP-5 is MIL-T-5624 and is standardized with those of other North Atlantic Treaty Organization (NATO) nations. The NATO name for this fuel is

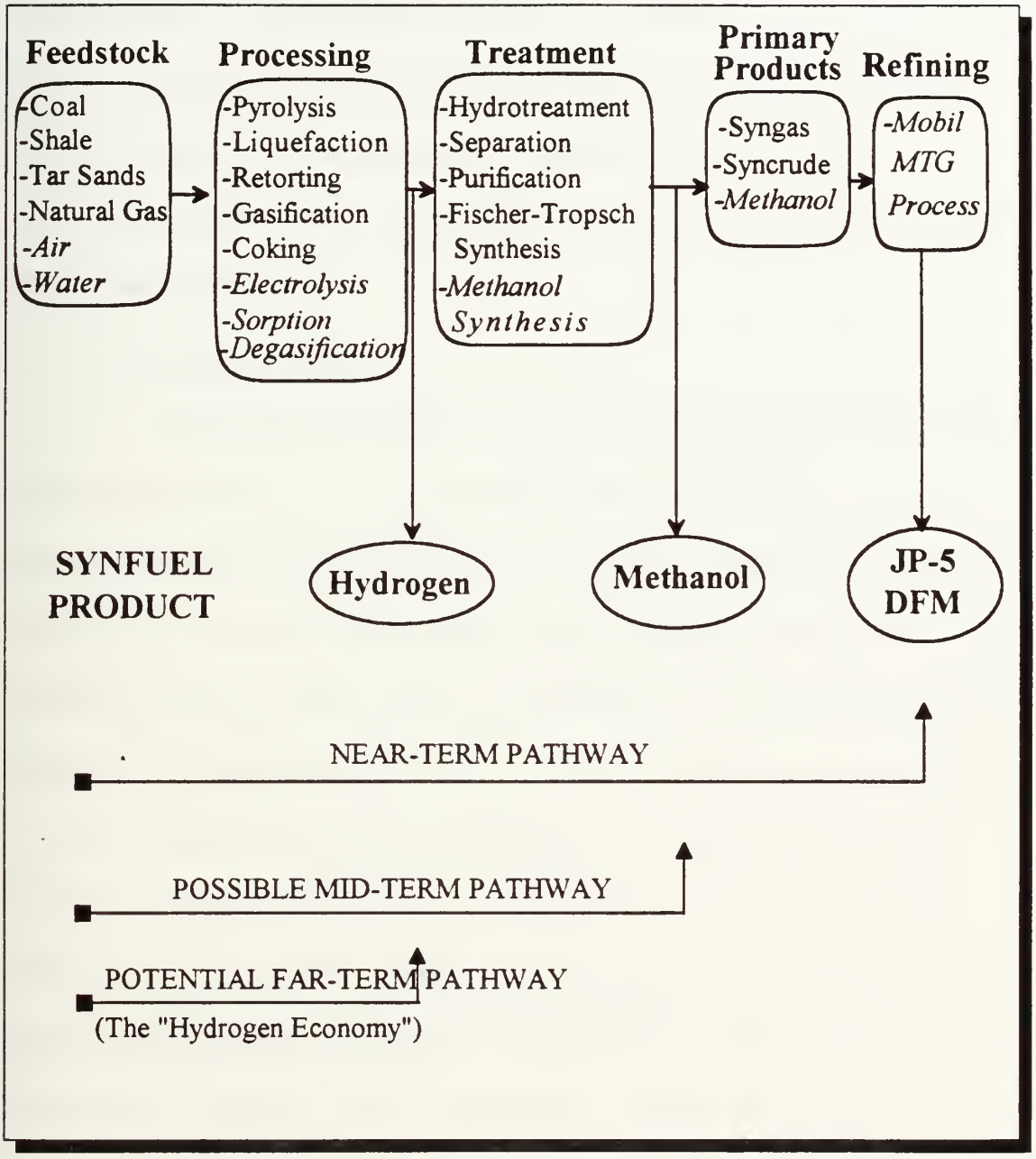


Figure 3.1
Pathways for Alternative Fuels

(Note: italicized entries are those of current interest)

F-44. It is a kerosene type fuel with a flashpoint of 60°C (140°F) (N-4). The higher flashpoint and other specific characteristics of JP-5 were developed to allow it to be safely stored aboard ships. Other aviation gasolines and JP-4, which is predominately used by the U.S. Air Force, have a much lower flashpoint (between -3.8°C (25°F) and -17.8°C (0°F)) and are more hazardous fuels for naval application. JP-5 is also similar in composition to ASTM 1D fuel, a volatile distillate fuel (H-4). More specific properties of JP-5 are listed in Table 3.2.

3.2.2 Diesel Fuel Marine

Diesel Fuel Marine (DFM) is the predominant fuel used by the U.S. Navy for ship propulsion plants. It is a very versatile fuel that is used in diesel, gas turbine and steam boiler power plants. It is composed of light to medium distillates (N-2). Although the common name for this fuel is still DFM, its correct title is Fuel, Naval Distillate. The MILSPEC for this fuel is MIL-F-16884 and is standardized with those of other North Atlantic Treaty Organization (NATO) nations. The NATO name for this fuel is F-76; F-76 is also recognized as a marine fuel internationally. In addition to NATO, the Southeast Asia Treaty Organization (SEATO) and the Central Treaty Organization (CENTO) also recognize F-76. Furthermore, most international and domestic oil companies are familiar with F-76 which is the acceptable name rather than DFM or Fuel, Naval Distillate. F-76 is also similar in composition to ASTM 2D fuel, a distillate fuel oil of lower volatility (H-4). F-76 has a minimum flashpoint of 60°C (140°F), which is also a minimum for all marine applications (N-4, H-4). More specific properties of DFM are listed in Table 3.2.

Table 3.2
Properties of DFM and JP-5
(taken from reference H-4)

	DFM	**JP-5**
Flashpoint (^{0}F)	140	140
Sulfur, $(\%)_{max}$	1	0.4
Lower heating value $(Btu/lb)_{min}$	18,190	18,300
Distillation end point $(^0F)_{max}$	725	550
Cetane Number	45	45
Residue $(\%)_{max}$	2	1.5
Density (kg/m^3)	788 - 845	788 - 845

3.2.3 Methanol

Many believe methanol will be the transportation fuel of the future. It is an excellent transport fuel, and can be used in both spark and compression ignition engines (M-6) as well as in gas turbines (O-6). For the near-term application, methanol is a intermediate product between CO_2/H_2 and the final end product JP-5 or DFM, as seen in Fig. 3.1. The belief that methanol will replace petroleum as the dominant transportation fuel has several explanations: methanol can be produced from a large number of materials, many of which are abundant in the U.S.; it can be made less expensively than almost any other alternative fuel option; it burns cleaner than petroleum fuels; and lastly, it is similar to gasoline and diesel fuel, therefore it will not require major and costly changes for the current transportation fuel operating and distribution systems (S-14).

Blending methanol with JP-5 or DFM should also be considered to extend their supplies in much a similar manner as M85 fuel is presently formulated (85 % methanol and 15 % gasoline). The benefits of this alcohol-gasoline blend are twofold: a leaner burning engine which produces less hydrocarbons and CO emissions and an engine with higher thermal efficiency (P-6). In addition to M85 fuel, methyl tertiary butyl ether (MTBE) is another blending agent which can be synthesized from methanol. MTBE, an oxygenated additive, has been used in recent years to reduce hydrocarbon, CO, and nitrogen oxide emissions in many urban areas of the U.S. as well as an octane booster. Methanol can also be used as a direct replacement for diesel fuel. Auto-ignition difficulties with methanol in diesel engines were first seen as a major drawback, however research efforts have since

solved this problem and today many countries operate fleets of methanol fueled trucks and buses.

Probably the most recent use of methanol in the transportation industry is with the flexible fueled vehicles (FFVs). These vehicles are the direct result of regulatory pressures and mandates from the state of California to reduce their rate of harmful emissions. FFVs can operate on either methanol, gasoline, or a combination of the two.

Another product derived from methanol is dimethyl ether (DME). Mentioned in chapter 2, DME is the first intermediate product in the dehydration of methanol as shown below.

$$2CH_3OH \Rightarrow CH_3OCH_3 + H_2O \qquad (3\text{-}3)$$

Researchers at the Haldor Topsoe laboratory in Denmark in collaboration with Amoco and Navistar (a diesel engine manufacturer) are investigating the use of DME in diesel engines (E-2). Exhaust from a DME fueled diesel engine contains zero sulfur, no soot and only about 25 % of the nitrogen oxides of a normally fueled diesel engine. Use of DME in diesel powered transportation could therefore make those vehicles easily pass the strict California emission standards planned for implementation in 1998, as well as elsewhere (E-2). Methanol provides such excellent power output and efficiency that it has been the only fuel used for Indianapolis 500 auto racing since 1965.

Methanol, either as a fuel or a chemical feedstock, is increasing in importance as witnessed by its world production capacity almost doubling in the last decade. This rapid growth and the lack of accurate data on methanol, has led the International Union of Pure and Applied Chemistry (IUPAC) to recently publish the thermodynamic properties of

methanol to assist in improving the design of new processes and equipment (R-2). Lastly, methanol as a naval fuel is extremely beneficial in the undesired event of a shipboard fire. The methanol flame possesses a low radiant heat output allowing firefighters a closer approach to the fire and a much lower probability of spreading the fire to adjacent ignitable materials (S-16). More specifics of methanol are listed in Table 3.3.

3.2.4 Hydrogen

Hydrogen as a fuel for naval propulsion, and in general as a transportation fuel, should be seriously considered as an alternative fuel for the long-term future. It is a clean burning and high energy value fuel with a lower heat of combustion of 120,000 kJ/kg (51,672 Btu/lb). More specifics of hydrogen are listed in Table 3.3. Many predict that hydrogen will be the energy medium for the long term, however, it will require a major paradigm switch from the conventional transportation fuels. It is one form of renewable energy that is attracting a great deal of research due to the abundance of water and solar energy, as well as its capability of being formed from coal, natural gas, and petroleum. Considerable literature is available (B-7, B-8, J-2, S-3) that discusses the future "hydrogen economy" or even a "solar hydrogen economy" with the use of photovoltaics as the power source. The motive for production of hydrogen for the present application is two-fold: first combined with CO_2 to form methanol, and secondly it can suffice as an alternative fuel itself.

Since the Hindenberg hydrogen airship tragedy in 1937, hydrogen has been regarded as an unsafe fuel or material. Although that disaster was eventful, it should be recognized that propulsion fuels used today for modern vehicles are all potentially

Table 3.3
Properties of Methanol and Hydrogen

	Methanol	**Hydrogen**
Density kg/m^3 (lb/ft^3)	788 (49.2)	71 (4.43) *Liquid* 0.09 (0.006) *Gas*
Energy value kJ/kg (Btu/lb)	20,000 (8,600)	120,000 (51,590) LH_2
Energy value MJ/m^3 (Btu/ft^3)	16,000 (429,900)	8,500 (228,500) LH_2

dangerous and involve some risk with their use. It is not commonly known that H_2 as a fuel is no more dangerous than gasoline, and after all, everyone in today's modern society accepts the risks of filling the tank and driving a gasoline powered automobile. A study comparing the relative safety of hydrogen, methane (CNG) and gasoline concluded that none of these fuels is inherently safer than the others (O-4).

The use of H_2 as an aircraft propulsion fuel is most realistically still 50 years away. Reference O-4 reports that using liquid hydrogen (LH_2) rather than jet fuel would reduce the fully loaded takeoff weight of a jumbo jet by about 25 %, which leads to a fuel savings of 12 %. However, presently the cost of liquefication and storage is high and estimated to be 50 - 65 % of the total cost of LH_2 making LH_2 roughly three times costlier than jet fuel. Gaseous H_2 used without liquefaction is only about one and a half times costlier than jet fuel, but requires heavy high pressure storage vessels. Therefore pure economics overshadow the meager energy savings possible with LH_2. Current naval aircraft (for aircraft carrier use) are smaller in size than commercial aircraft and should therefore be expected to not benefit from LH_2 fuel use unless there are major changes in aeronautical design. Reference B-6 describes studies of three different types of military aircraft fueled with LH_2: the conceptual High Altitude Long Endurance (HALE) aircraft, the Navy's land-based P-3 Antisubmarine Warfare (ASW) aircraft, and the conceptual transport aircraft including PAR-WIG designs for surface effect aircraft. On the positive side there is a long and successful history with the use of hydrogen as a rocket and space shuttle propellant in the NASA program.

The use of hydrogen as a transportation fuel can be illustrated with a few examples of present day R&D. The Russian aircraft manufacturer Tupolev, and Deutsche Airbus have been studying the use of liquid hydrogen in their "Cryoplane" project (H-3). Tupolev is currently using similar cryogenic technology in constructing three cargo airliners to be powered by liquid natural gas (LNG). It is expected that Tupolev's use of LNG is a precursor to ultimate fueling using hydrogen. The German carmaker Bavarian Motor Works (BMW) announced a demonstration tour of North America in 1995 for their liquid hydrogen powered internal combustion sedan. Eager to attract the market niche for zero emission vehicles (ZEV) in California and Canada, BMW predicts a strong future for hydrogen powered vehicles. Their corporate vision is certainly for the future and are quoted as saying "The technology is ready for practical use" and "hydrogen fueled engines are no longer a long-term dream, but a practical possibility" (H-3).

3.3 Propulsion Plant Selection

The prime mover or propulsion plant for naval aircraft or ships must be reliable, efficient, and compact. After all, the chosen propulsion plant has a direct effect on the weight, size, cruising range, speed, and maneuverability of the vessel (S-4). Reference S-4 was a comprehensive and recent review of naval propulsion systems with particular emphasis on the uses of improved technology for naval applications. This reference, as well as references J-1 and H-4, were utilized to provide a basis of currently available naval propulsion systems and what will be "technologically available" in the future, be it mid-term or long-term. Propulsion plants briefly discussed below are the present day steam turbine, diesel engine, and gas turbine and for the future, fuel cells and electric

drive. It is not intended to fully describe the complete cycles and operations, but rather provide an introduction of various users (propulsion plants) for the synthetic fuel which is to be generated. Table 3.4 shows the propulsion plants to be discussed.

3.3.1 Steam Turbine

The steam turbine is presently used in the U.S. Navy on board some older fossil fueled ships as well as nuclear powered aircraft carriers, cruisers, and submarines. The role of the steam turbine power plant in today's modern Navy is diminishing due to both the downsizing of the military and the desire to propel all new ships with gas turbines or diesels. However, the conventional steam plant is a proven technology and offers the ability to use a wide range of hydrocarbon based fuels. The nuclear steam plant is essentially the same as the conventional plant, although the boiler is replaced by a nuclear reactor plant. The boiler for the conventional power plant burns fuel to make heat energy available. Naval boilers burn Fuel, Naval Distillate (DFM) and can burn JP-5 if desired since both are light fuels. Specific characteristics and advantages/disadvantages of the steam turbine power plant are listed in Table 3.4.

3.3.2 Diesel Engine

The diesel engine is presently used in the U.S. Navy on board small vessels such as minesweepers, amphibious landing craft, and patrol craft as well as larger ships such as tenders, oilers and amphibious ships. Unlike the steam turbine power plant, it is a versatile power plant that needs little auxiliary support. Diesel engines for naval use are medium and high speed diesels. One advantage diesel power plants have over both steam and gas turbine power plants is that they operate at substantially lower rotational speeds,

Table 3.4
Naval Power Plant Characteristics

	Efficiency	Specific Fuel Consumption (SFC) lb/SHP-hr	Advantages	Disadvantages
Steam Turbine	25% - 34%	0.42 - 0.47	• Technologically developed • High reliability • Wide range of fuels • Power over wide range of loads	• Low Efficiency • High SFC • Air/thermal pollution • High manning • Long heat-up required
Diesel	36% - 48%	0.34 - 0.38	• Low cost • Low SFC • High reliability • High efficiency • Technologically developed	• Large weight • Large size • Air/thermal pollution
Gas Turbine	32% - 42%	0.35 - 0.65	• High reliability • Low specific weight • Reduced manning • Less air pollution	• Large intakes and exhausts • Harsh marine environment can damage • Low efficiency at partial load
Fuel Cell	65% - 80%	H_2 consumption: 0.111 lb/kWh O_2 consumption: 0.889 lb/kWh (see note)	• High efficiency • No pollution • No moving parts • Reduced manning • Very low maintenance	• Costly • Lack of precedent for maritime use • High specific weight • H_2 storage problems

Note: Taken from reference C-9 for a 1000 kW PEM fuel cell at full power.

which allows a smaller reduction gear to be utilized. A principal disadvantage unique to diesels however is their excessive consumption rate of lubrication oil, which can be as high as 5% of the fuel consumption (S-4). Like fuel, additional lubrication oil must therefore be carried on board to compensate.

Obviously, the naval diesel engine uses naval distillate fuel, commonly referred to as DFM. However, as mentioned earlier, JP-5 can be used successfully in diesel engines which enables simplification of logistics problems since a fleet at sea also uses JP-5 for gas turbine powered (i.e. jet engine) aircraft. The increased cost of JP-5 is offset by the advantage of having to carry only one grade of fuel in tankers or oilers (H-4).

3.3.3 Gas Turbine

The gas turbine power plant is the U.S. Navy's modern day engine for a large majority of combatant ships, as well as for aircraft. Regardless of whether the gas turbine is used for aircraft propulsion or as the aircraft engine derivative used for ship propulsion, both operate similarly and use JP-5 as fuel (the ship variant gas turbine predominately uses DFM due to cost). An advantage particular to ship propulsion is that the gas turbine power plant is usually installed in modules. The modular construction greatly facilitates installation and removal as well as providing a first line of defense against fire or structural failure (S-4). Sodium and vanadium are especially corrosive to the gas turbine. Sodium is always present in a marine environment in seawater and vanadium is frequently present in lower grades of fuel, like residual fuel (H-4). As a result the specifications for gas turbine fuels, either JP-5 or DFM, are more demanding than for other transportation fuels.

3.3.4 Fuel Cells

A fuel cell is an electrochemical device that offers high efficiency and environmental benefits, and which converts chemical energy into electrical energy. Various feedstocks can be utilized, such as methanol or fuel oil, however a reformer is then required to split the H_2 from the feedstock. This makes the process less efficient and more complex than merely using H_2 as the fuel directly. Therefore, for obvious reasons, if fuel cells are to be envisioned for a naval application, H_2 will probably be the fuel of choice due to space and weight constraints. Commercially fuel cells are presently attracting considerable attention and reference H-8 reports that there were approximately 259 phosphoric acid fuel cell power units, 35 molten carbonate fuel cell stacks, and 12 solid oxide fuel cell modules operating worldwide in 1994, for a total capacity of 48 MW_e. Land based applications of fuel cells are rapidly increasing. In March 1994, the U.S. Army and Air Force purchased twelve 200 kW_e phosphoric acid plants built by the ONSI Corporation, a subsidiary of International Fuel Cells. The Miramar Naval Air Station in Southern California is the site of a 250 kW_e molten carbonate demonstration plant for M-C Power and San Diego Gas and Electric.

Thus far, fuel cells primarily have been utilized for small scale commercial power plants, in the NASA space program, and also limited use in the transportation sector as an engine for low emission vehicles (LEVs). However, their quiet operation and high efficiency makes fuel cells potentially attractive power sources for naval surface ships and submarines (S-4). Furthermore, for the proposed naval synthetic fuel plant, the final product could be hydrogen, in which case only the electrolysis plant is required. In

addition to the aforementioned fuel cells, the proton exchange membrane (PEM) fuel cell is one which operates at a maximum of 95 ^{0}C (200 ^{0}F) and is more favorable than the other designs for mobile applications, at least until the noble metal catalyst production fails to keep pace with the PEM production (A-2). The largest single autonomous underwater vehicle (AUV) development project currently underway is being administered by the Defense Advanced Research Project Agency (DARPA) for the U.S. Navy (H-8). They have examined numerous power systems and concluded that only electrochemical power systems, particularly PEM fuel cells, are the best technology for the mission.

The last fuel cell to introduce is the alkaline fuel cell (AFC) which has become fully developed and the best performer, although its use has been limited to the Space Shuttle orbiter. AFCs operate at low temperatures (~80 ^{0}C) which produces waste heat insufficient to produce steam for reforming fuel, therefore AFCs are best suited to being fueled with hydrogen directly. The lower temperatures are advantageous since inexpensive plastics can be used for manufacturing the cell package, which greatly reduces the overall weight. The projected weight of 1 kg/kW (2.2 lb/kW) makes it attractive for vehicle applications (A-2).

3.3.5 Electric Drive

The use of electric drive for ship propulsion is not a new concept but one that has been utilized on board the U.S. Navy's first aircraft carrier, Langley, as well as other large World War II era Navy vessels. Furthermore, the cruise ship Queen Elizabeth II recently was converted from a geared steam turbine drive to diesel electric drive (S-4). Presently the U.S. Navy, under the auspices of the Advanced Surface Machinery Program

(ASMP), and with the assistance of Westinghouse, has an integrated electric drive (IED) system that is fully designed and awaiting implementation . Reference A-3 contains an excellent summary of past, present and future marine electric drive systems.

Electric drive motors of today are based on techniques which were established in the early 20th century. These traditional approaches can not be expected to be significantly further improved and therefore some fundamental changes have to be undertaken (A-3). One hopeful prospect is using zero resistance superconducting coils and windings. The understanding and improvements made with superconducting motors and generators offers great promise for utilization in marine electric drive. Superconducting technology reduces the size and weight of the machinery, as well as providing a 5 % to 10 % improvement in the electric drive efficiency. Although electric drive is less efficient then the currently used mechanical drive, it offers better arrangement flexibility to enhance ship survivability and enhance design and construction (S-4). Therefore, the Navy's "all electric" ship should be realized to be a viable mid-term endeavor. With an electric ship, such as an aircraft carrier, the required electric power is readily available for operating a synthetic fuel plant in parallel with ship propulsion. Hence electric drive for the U.S. Navy can only enhance the application of synthetic fuel generation.

3.4 Summary

This chapter focused on the naval applications of a synthetic fuel product. The product is envisioned to have many forms, such as synthetic JP-5 and DFM for the near-term, methanol for the mid-term, and hydrogen for the long-term. The technology is currently available to produce synthetic JP-5 and DFM and allow direct use of methanol

or hydrogen in the future. Naval propulsion plants should also be expected to change, and an "all electric" Navy with fuel cells and electric drive is possible. Hydrogen fueled naval aircraft are also possible. The improvements in fuels and energy conversion mechanisms are all consistent with an effort to provide a more energy independent and efficient naval force at sea.

Chapter 4

NAVAL SYNTHETIC FUEL PRODUCTION PLANT

4.1 Introduction

Earlier chapters developed the premise of utilizing hydrogen and carbon dioxide for synthetic fuel generation. This chapter discusses the sources for H_2 and CO_2 as well as processes to obtain them. Once obtained they can undergo methanol synthesis and MTG processes to ultimately produce the final product, JP-5. Lastly, fundamental energy requirements are established to size the plant for installation on board a naval vessel, for use in chapter 5.

4.2 Hydrogen Generation

The production of hydrogen is vital for methanol synthesis. As will be shown later, it is the most energy intensive of all the processes involved in the production of a synthetic fuel. Coal gasification and steam reforming of natural gas are the most extensively used industrial processes to produce hydrogen today. However, as discussed in Chapter 1, the use of fossil fuels is not a long-term alternative for hydrogen production due to environmental effects and/or limited fossil fuel reserves. Figure 4.1 shows the principal possibilities for producing hydrogen from non-fossil sources such as nuclear and solar. The focus of hydrogen production for naval purposes will be predominantly water electrolysis; however, other non-fossil processes will be discussed, such as thermo-chemical and solar energy.

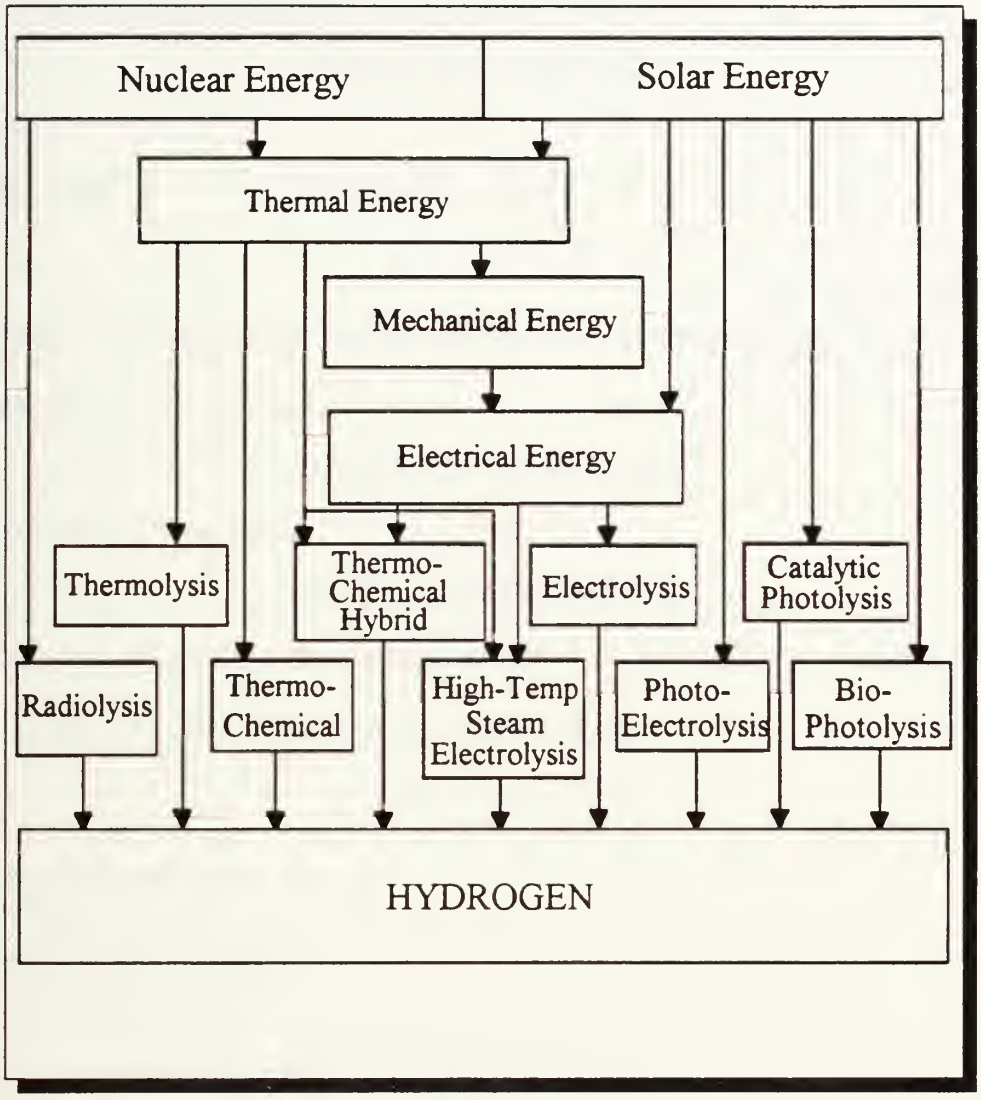


Figure 4.1
Energy conversion processes for non-fossil hydrogen production

4.2.1 Electrolysis

Fundamentally, hydrogen can be produced from water by separating H_2O into H_2 and O_2 with the addition of energy. This is shown by:

$$H_2O \Rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad (4\text{-}1a)$$

or alternatively,

$$H_2O \Rightarrow \tfrac{1}{2}O_2 + H_2 \qquad (4\text{-}1b)$$

Actually in the electrolytic cell two half cell reactions are occurring simultaneously.

The cathodic half cell reaction is:

$$2H_2O + 2e^- \Rightarrow H_2 + 2OH^- \qquad (4\text{-}2)$$

The anodic half cell reaction is:

$$2OH^- \Rightarrow \tfrac{1}{2}O_2 + H_2O + 2e^- \qquad (4\text{-}3)$$

The theoretical energy input (free energy) to effect this electrolysis reaction, like many others, is affected by temperature, as shown by Gibbs law:

$$\Delta G = \Delta H - T\Delta S \qquad (4\text{-}4)$$

where:
ΔG =free energy (kJ/mol)
ΔH =enthalpy (kJ/mol)
T =reaction temperature (°K)
ΔS =entropy (kJ/mole°K)

Since ΔH and ΔS are approximately constant with temperature (P-9), they may be replaced by their standard state values, ΔH^0 and ΔS^0. Then since $T\Delta S$ increases with temperature, ΔG will decrease with increasing temperature. Therefore, if higher temperatures are utilized, less electrical energy is required.

Principally, there are three different processes developed for electrolytic water dissociation: alkaline aqueous electrolysis, solid polymer electrolysis or membrane

Table 4.1
Cell Specifications for Several Commercial Electrolyzers

Manufacturer	**Electrolyzer***	**BBC****	**Norsk Hydro****	**de Nora****	**Lurgi****
Cell Type	Unipolar	Bipolar	Bipolar	Bipolar	Bipolar
Pressure	Ambient	Ambient	Ambient	Ambient	3 MPa (29.6 atm)
Temperature (°C)	70	80	80	80	90
Current density (kA/m^2)	2.5	2	1.75	1.5	2
Voltage (V)	1.85	2.04	1.75	1.85	1.86
O_2 purity	99.7	>99.6	99.5	99.6	99.4
H_2 purity	99.9	>99.8	98.85	99.9	99.85
Energy kWh/m^3 H_2	4.4	4.9	4.3	4.6	4.5

* denotes taken from reference S-15
** denotes taken from reference W-1

electrolysis, and high temperature steam electrolysis. Alkaline aqueous is by far the most common and is a well established technology. It employs an asbestos diaphragm separating the electrodes and usually uses an alkaline electrolyte such as potassium hydroxide (KOH). Table 4.1 summarizes typical operating data for a number of different manufacturers (W-1 and S-15). As seen in Table 4.1, all but one manufacturer use bipolar electrodes. Bipolar electrolyzers have the individual cells linked electrically and geometrically in series. The Stuart cell, of Electrolyzer Inc., is a unipolar design whereby the individual cells are connected in parallel, which is unique to the entire electrolyzer industry. The manufacturing advantages of the unipolar design are: rugged and simple design, higher current density and therefore higher coulombic efficiency than bipolar designs, longer service life, and modular design (S-15). Additionally, unipolar electrolyzers are currently less expensive than bipolar electrolyzers (J-2). For the present purposes, since alkaline water electrolysis is a well proven technology, it will be used for the naval synthetic fuel plant. Specifics for this hypothetical electrolyzer are:

Operating temperature	70°C
Operating Pressure	Atmospheric
Hydrogen purity	99.9 %
Hydrogen yield	99.9 %
Energy required	4.4 kwh/m^3 H_2
Energy Efficiency	80 %

The energy requirement is the most significant specification; it falls within the range of the commercially available electrolyzers listed in Table 4.1. This is supported by reference M-5, which states that the energy consumption for a "conventional" electrolyzer

is 4.8 kwh/m^3, and that for an advanced alkaline technique is 3.9 kwh/m^3. Since 4.4 kwh/m^3 is within this range it will be used. Achieving higher efficiency and lower cost with advanced alkaline electrolyzers will require the following: a zero gap cell, new diaphragm materials, and electrocatalysing electrode surfaces, all of which are too advanced and not well proven for application at the present time. However, they should be considered in the future to reduce the energy consumption for the hydrogen generation process.

The solid polymer electrolyte (SPE) process uses the high electrolytic conductivity of a proton loaded membrane, such as nafion. Membrane technology, like SPE, is not any better than the advanced alkaline electrolysis process and has been regarded as well proven for a number of years (W-1). For this reason, and its small capacity, it is not useful for this application. Likewise, steam electrolysis is ruled out due to the required high operating temperature (800 - 1000 °C) and material and fabrication difficulties which are still unresolved (W-1). Only small laboratory scale cells have been tested and because of the many difficulties encountered, commercial use of high temperature steam electrolysis is still far away (J-2). Obviously, once proven, the high temperature steam electrolysis process could be extremely beneficial in conjunction with a high temperature gas cooled reactor (HTGR).

4.2.2 Thermal-Chemical

A recent program launched by H-Power Corporation produced hydrogen , on a small scale, by reacting sponge iron with steam (J-2). The overall chemical reaction is given by:

$$3Fe + 4H_2O \Rightarrow Fe_3O_4 + 4H_2 \qquad (4\text{-}5)$$

The steam oxidation reaction occurs at a temperature between 25-900 °C (77-1652 °F) although temperatures above 500 °C require no catalyst. H-Power's research is oriented toward providing H_2 for fuel cells without the difficulties and expense of storing and transporting gaseous or liquid hydrogen. However, raw sponge steel is required as a feedstock (as well as steam). In the present application this would have to be regenerated from iron oxide on board if self sufficiency is to be preserved. Prospects for doing this are unlikely.

Other thermo-chemical processes that have received more research and are better known are the Westinghouse sulfur cycle (Mark 11), the Ispra Mark 13 bromine-sulfur cycle and the General Atomic iodine-sulfur cycle (B-10 and W-1). These cycles all require very high temperature, in the range 950-1150 °C (1742-2102 °F), and utilize the principle of thermolysis and electrolysis to yield elemental hydrogen. The thermolysis reaction decomposes sulfuric acid (H_2SO_4) to sulfur dioxide (SO_2) which is used in a lower temperature electrolysis reaction to split off hydrogen from water. There has been much interest by HTGR proponents in this cycle. References H-7 and P-5 are but a few of the related studies. Even if perfected, the use of noxious, corrosive chemicals, as well as system complexity would probably preclude use of most of these processes on board ship.

Therefore, due to the lack of experience with thermo-chemical processes and their associated material difficulties, and the desire to utilize existing PWR technology (at $< 300\ ^{0}C$), these processes will not be considered for use at this time.

4.2.3 Solar Energy

Production of hydrogen from solar energy, as shown in Fig. 4.1, is possible by photoelectrolysis, catalytic photolysis, bio-photolysis, and the use of photovoltaic cells as an electric source for conventional electrolysis. All are useful and well researched processes that have been demonstrated on a small scale. However, as a naval application the energy conversion mechanisms and process equipment are too large, primarily because of the diffuse nature of sunlight (<1 kW/m^2), and furthermore do not lend themselves to providing a dependable and mobile source of hydrogen. Additionally, it appears that there are no economies of scale to achieve in photovoltaic hydrogen production beyond a relatively modestly sized 5 to 10 MW_e facility (O-4). Work partially funded by the Office of Naval Research investigated producing hydrogen from seawater using a semiconductor septum electrochemical photovoltaic (SC-SEP) cell, which was modeled after nature's photosynthetic thylakoid membrane (T-1). However it is anticipated that the volume of hydrogen generated by such a process will be only a small fraction of what is required for methanol synthesis.

4.2.4 Energy Demand

The energy demand for the generation of H_2 can be easily determined from the ΔG for electrolysis of water:

$$2H_2O_{(l)} \Rightarrow 2H_{2(g)} + O_{2(g)} \qquad \Delta G_{electrolysis} = 56.7 kcal/gmole \tag{4-6}$$

The ΔG is equivalent to 237.3 kJ/gmole of H_2. Since ΔG for electrolysis is referenced to 25°C and 1 atmosphere, it can be converted to a volumetric basis knowing that there are 0.0224 m^3/gmole for a gas at standard temperature and pressure (STP). This yields a

value of 2.94 kWhr/m^3 H_2 (83.4 kWhr/1000 ft^3). Using the energy requirement for the standard hypothetical alkaline electrolyzer stated earlier of 4.4 kWhr/m^3 H_2 results in a 67 % efficiency, which is less than the published data for electrolyzer performance. The value of 4.4 kWhr/m^3 H_2 must therefore also include pumping and other ancillary equipment energy. As noted earlier a reasonable efficiency for present day alkaline electrolyzers is 80 %. Thus the actual energy requirement to make H_2 will be taken as 3.7 kWhr/m^3 H_2 (2.94/0.80) in the present study. Ancillary energy requirements will be accounted for elsewhere.

4.3 Carbon Dioxide Generation

4.3.1 Sources of Carbon Dioxide

Carbon dioxide is present everywhere in the environment: including the atmosphere, oceans and geological formations. The most ubiquitous source of CO_2 is the atmosphere. However, the vast amount of ocean waters are in constant exchange with the atmosphere and are a large sink for CO_2.

Atmospheric CO_2 concentration in 1988 was reported as 350 ppm, a value predicted to increase at a rate of 1.5 ppm per year (B-3). Although many current estimates for atmospheric CO_2 concentration are higher than 350 ppm, 350 ppm is a conservative estimate for these scoping calculations.

The ocean (seawater) contains even more CO_2 than is contained in the entire atmosphere, in fact, 62 times more (S-17). Seawater contains CO_2 in the form of bicarbonate (HCO^{-1}_3) ions, carbonate (CO^{-2}_3) ions, carbonic acid (H_2CO_3) and undissociated CO_2 molecules all in equilibrium (H-10). Of these, approximately 90% of

the CO_2 in the seawater is in the form of bicarbonate, 9 % as carbonate, and only 1 % as molecular CO_2. In accord with common practice, we will quote content as total CO_2 regardless of form. The CO_2 concentration in seawater is dependent upon location, pH, salinity, pressure and temperature. With a constant pH, the CO_2 concentration increases with salinity, and decreases with temperature. Therefore, as the ocean depth is increased the temperature, pressure and salinity effects all cause a higher CO_2 concentration (CO_2 concentration at 4 km (13,100 ft) is 17 % higher than at the surface). Although the seawater CO_2 concentration is variable, a conservative value of 100 ppm will be used for these scoping analyzes.

Geological formations or fields containing natural gas resources also are laden with CO_2. Although the main component of natural gas is methane (CH_4) it often contains inert non-hydrocarbon gases such as nitrogen, helium and carbon dioxide. CO_2 in natural gas typically can be found in concentrations of up to 60 % (N-6). Recently, efforts are in progress to utilize the Natuna gas field in the southern South China Sea to eventually supply LNG to Japan, South Korea and Taiwan (O-7). This field however, contains approximately 71 % CO_2 and 28 % methane. The CO_2 removal process would be performed at sea on the drill platforms using proven industry experience in low temperature gas separation. Similar to other oil and natural gas fields, some CO_2 could be used for enhanced oil recovery (EOR) to further exploit the field. However due to the vast amount of CO_2 (4 trillion m^3 (149 trillion ft^3)) it is reported that the excess CO_2 will be pipelined for injection into carbonate aquifers (O-7). The Natuna field is in close

proximity to Singapore and could possibly be a long term source of CO_2 for a forwardly deployed naval synthetic fuel plant.

Currently the most wide scale and heavily researched area concerning CO_2 is with its removal from the stack (flue) gas of fossil fueled industrial power plants. References P-7 and P-8 contain numerous articles discussing the present applications for removing and disposing of stack gas, particularly CO_2. CO_2 capture from stack gas can be performed by one of the following common processes: pressure swing adsorption (PSA), amines such as monoethanolamine (MEA) absorption, microalgal photosynthesis, membranes, and molecular sieving. Therefore, CO_2 scrubbing of stack gas can potentially be a viable source of CO_2 for a land-based synthetic fuel plant, particularly if the fossil fuel plant is co-located with a nuclear power plant.

4.3.2 Carbon Dioxide Separation From Air and Seawater

The supply of CO_2 for a naval synthetic fuel plant can best be derived from the atmosphere (air) or from seawater, since either are ubiquitous sources. When compared to the major constituents of air, nitrogen (78 %) and oxygen (21 %), CO_2 has a much greater concentration in seawater then either of them. Seawater with a salinity of 35,000 ppm in equilibrium with the atmosphere at 15^0C (59^0F) contains approximately 13 ppm of dissolved N_2 and 8 ppm of dissolved O_2 (H-10), compared to a CO_2 concentration of 100 ppm. Furthermore, note that the concentration of CO_2 in pure fresh water is only about 0.5 ppm.

Table 4.2
Summary of CO_2 Separation Processes Evaluated for Methanol Production
(taken from reference S-8)

Process	CH_3OH Production (bbl/day)	Capital ($/bbl/day) 1975 dollars	Energy for CO_2 Separation (kW_eh/lb)	Total Energy for CH_3OH (kW_eh/lb)	Total Energy for H_2 (%)
CO_2 from Air by Absorption/Stripping with Water at Atmospheric Pressure	18,600	4,282	1	4.5	67
CO_2 from Air by Absorption/Stripping with Cooling Tower at Atmospheric Pressure	19,700	2,920	0.78	4.28	63
CO_2 from Air by Absorption/Stripping with Water at High Pressure	63,422	25,200	9.66	13.16	27
CO_2 from Air by Absorption/Stripping with Methanol at High Pressure and Low Temperature	7,721	24,000	7.31	10.81	32
CO_2 from Air by Refrigeration and Water Vapor from Air by Adsorption on Molecular Sieves	9,200	25,700	7.21	10.71	33
CO_2 and Water Vapor from Air by Refrigeration	6,600	40,000	9.14	12.64	28
CO_2 from Air by Absorption/Stripping with Aqueous K_2CO_3 at Atmospheric Pressure	21,400	2,082	0.4	3.9	90
CO_2 and Water Vapor from Air by Adsorption/Desorption on Molecular Sieves	8,700	14,460	6.1	9.6	34
CO_2 from Seawater	21,700	1,146	0.35	3.85	91

Reference S-8 was the result of an exhaustive study to determine the feasibility of separating CO_2 from the atmosphere or seawater for use in producing methanol. Table 4.2 summarizes this work and shows that separating CO_2 from seawater required the lowest capital investment and lowest energy requirement when compared with the other eight air separating technologies. However, reference S-8 recommended the use of an aqueous potassium carbonate (K_2CO_3) solution for the absorption and stripping of atmospheric CO_2. This choice was made to allow siting of the synthetic fuel plant anywhere, without the need for the availability of seawater. Obviously, the extraction of CO_2 from seawater is of much higher interest for use in a naval synthetic fuel plant.

To further show the advantages of the extraction of CO_2 from seawater compared with atmospheric CO_2 the following analysis is provided. The work required to pump any fluid, water or air is proportional to the product of the volumetric flowrate and the pressure drop.

$$W \propto V \times \Delta P \tag{4-7}$$

where:
W = pumping work (kW)
V = volumetric flowrate (m^3/sec)
ΔP = pressure drop in apparatus (Pa)

and $$\Delta P \propto \rho \times v^2 \tag{4-8}$$

where:
ρ = fluid density (kg/m^3)
v = flow velocity (m/sec)

substituting yields: $$W \propto \rho \times V \times v^2 \tag{4-9}$$

but: $$m = \text{mass flowrate (kg/sec)} = \rho \times A \times v = V \times \rho \tag{4-10}$$

therefore: $$W \propto \frac{m^3}{\rho^2 \times A^2} \tag{4-11}$$

Define: $c = (f)(m)$

where:
c = process rate of CO_2 input (kg CO_2 per sec)
f = mass fraction of CO_2 in air or water

Thus the pumping energy (kJ) expended per unit mass (kg) of CO_2 processed is:

$$\frac{W}{c} \propto \frac{1}{f} \times \frac{m^2}{\rho^2 \times A^2} \propto \frac{v^2}{f}, \frac{kJ}{kg} \tag{4-12}$$

From the above equation it can be seen that if W/c and A are required to be the same for both water and air, the mass flowrate of CO_2 will be approximately 440 times larger in the water system since the density of seawater is approximately 830 that of air (actually 1025 kg/m^3 to 1.23 kg/m^3 at 15^{0}C (59^{0}F)) and the mass fraction of CO_2 100/350 lower. Conversely, if the same mass flowrate is assumed, the air system will be approximately 440 times larger than the water system. Hence recovery of CO_2 from seawater can, in principle, be done in a much more compact system: a major advantage for shipboard applications.

4.3.3 Energy Demand

Appendix D contains calculations for determining the energy requirement for obtaining CO_2 from seawater. Three processes were analyzed: single effect evaporator, vacuum/vapor compression evaporator, and a modified vacuum/vapor compression evaporator. The estimated energy consumption is 0.54 kWhr/kg CO_2 (835 Btu/lb CO_2). This is approximately the same as the total process energy cited in reference S-8 for CO_2 removal from seawater, which is reasonable agreement with our estimate in consequence of the lack of detail in both analyses.

4.4 Methanol Synthesis

Once carbon dioxide and hydrogen are obtained from the previous processes they can be combined in a heterogeneous catalyst reactor to produce methanol. The synthesis can be from either of the following chemical reactions.

$$CO_{(g)} + 2H_{2(g)} \Rightarrow CH_3OH_{(l)} \qquad \Delta H_{reaction} = -30.62 kcal/gmole \tag{4-13}$$

$$CO_{2(g)} + 3H_{2(g)} \Rightarrow CH_3OH_{(l)} + H_2O_{(g)} \quad \Delta H_{reaction} = -20.79 kcal/gmole \tag{4-14}$$

Both reactions are exothermic, and in the industrial production of methanol both reactions occur simultaneously. In the present analysis only CO_2 feed is employed, hence equation 4-14 will be used. The ΔH reaction is equivalent to -87.0 kJ/gmole of CH_3OH. Therefore it takes three moles of H_2 and one mole of CO_2 to produce 1 mole of methanol. Although the precise catalytic mechanisms will not be discussed, reference C-3 contains recent information about the generation of methanol. As mentioned in chapter 2, copper-zinc based catalysts are predominately used for methanol synthesis because they exhibit a high selectivity for methanol. Methanol yields are therefore high and generally result in greater than 99.5 % conversion. A low temperature and pressure conversion process is very desirable for this application. Recently Lurgi announced a "low" pressure methanol synthesis process which operates in the temperature range of 250 - 270 ^{0}C (480 - 515 ^{0}F) and pressure range of 40 - 100 bar (~600 - 1500 psia) (K-1). Test results indicate consistent conversion for methanol of, again 99.5 %, which is similar to Lurgi's and other high pressure (e.g. ~100 - 1000 bar) methanol synthesis plants. In the future even lower pressure catalytic processes can be expected as witnessed by Toshiba's experimental

development of a 10 bar (145 psia) methanol process, described in section 2.7.

4.4.1 Energy Demand

Since the reaction of H_2 and CO_2 is an exothermic reaction, methanol synthesis itself requires no net addition of energy, and returns energy in the form of steam for other uses in the plant. However the compression and heatup of H_2 and CO_2 feed for the reactor can not be overlooked.

The work required for adiabatic compression of a gas is given by:

$$kW = \frac{k}{k-1}\left(\frac{WRT_1}{1000}\right)\left(\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right) \qquad (4\text{-}15)$$

where:

k = 1.4 for H_2	k = 1.3 for CO_2
R = 4157 J/kg^{0}K for H_2	R = 189 J/kg^{0}K for CO_2
T_1 = 343 ^{0}C for H_2	T_1 = 300 ^{0}C for CO_2
P_2 = 100 atm for H_2	P_2 = 100 atm for CO_2
P_1 = 1 atm for H_2	P_1 = 1 atm for CO_2
W = 1 kg/sec for H_2	W = 1 kg/sec for CO_2

This results in a pumping power requirement of 13,612 kJ/kg of H_2 which is equivalent to 3.8 kWhr/kg of H_2. The pumping power requirement for CO_2 is likewise 465 kJ/kg of CO_2 or 0.13 kWhr/kg of CO_2.

The heatup of H_2 and CO_2 is required to allow for the catalytic reaction for methanol synthesis. Hydrogen must be increased from 70 ^{0}C to 270 ^{0}C while CO_2 must be increased from approximately 27 ^{0}C to 270 ^{0}C. Multiplying the specific heat by the difference in temperature results in a heat input of 3075 kJ/kg of H_2 and 270 kJ/kg of CO_2.

4.5 Liquid Product

The liquid product, either JP-5 or DFM, results from methanol conversion. Described in chapter 2, the Mobil MTG process is one that appears very useful for naval

application. Since DFM is similar to JP-5, as shown in chapter 3, it will not be considered separately and the product JP-5 will be universally used. The overall reaction is shown below where $(CH_2)_n$ can be considered equivalent to JP-5 as described in appendix C.

$$nCH_3OH_{(l)} \Rightarrow (CH_2)_{n_{(l)}} + nH_2O_{(g)}, \quad \Delta H_{reaction} = -10.79 kcal/gmole \quad (4\text{-}16)$$

Again, note that this process is exothermic and that the heat of reaction is equivalent to -45.2 kJ/gmole. Similar to methanol synthesis, the reactant (methanol) must be heated to approximately 370 ^{o}C for this catalytic reaction. Fortunately, the sum of the heat of vaporization of methanol and the sensible heat required to bring methanol to the reaction temperature balances the heat of reaction and no net energy input is required for the MTG process.

4.6 Overall Energy Balance

Table 4.3 shows the energy requirements for each individual process in the proposed naval synthetic fuel plant on a per kilogram of $(CH_2)_n$ basis. Most of the energy is consumed in the form of electric energy. The thermal energy processes are the heatup of H_2 and CO_2 for methanol synthesis and the heatup of methanol for the MTG process. Since both methanol synthesis and MTG are exothermic reactions, the resultant energy generation can be utilized, with proper process design and optimization, to provide all the thermal energy requirements (heatup). Thus there is no net thermal energy input. The energy input in the form of electrical energy is assumed to be provided by a 25 % thermally efficient naval nuclear power plant, in which case the total thermal energy requirement is 87.6 $kW_{th}hr/kg$ of $(CH_2)_n$. Knowing that one barrel of $(CH_2)_n$ is

Table 4.3
Overall Energy Requirements

Process Step	Theoretical Energy (kWhr/kg of $(CH_2)_n$)	Efficiency of Process Step (%)	Predicted Process Energy (kWhr/kg of $(CH_2)_n$)	Notes
Electrolysis for H_2 generation	14.1	80	17.7	Section 4.2.4 (Electric)
CO_2 separation from seawater	1.7	90	1.9	Section 4.3.3 (Electric)
H_2 compression to 100 bar	1.6	90	1.8	Section 4.4.1 (Electric)
CO_2 compression to 100 bar	0.41	90	0.45	Section 4.4.1 (Electric)
H_2 heatup to 270 ^{o}C	0.37	N/A	0.37	Section 4.4.1 (Thermal)
CO_2 heatup to 270 ^{o}C	0.24	N/A	0.24	Section 4.4.1 (Thermal)
Methanol Synthesis	-1.7	N/A	-1.7	Section 4.4 (Thermal)
MTG	-0.9	N/A	-0.9	Section 4.5 (Thermal)
Total Electric Energy Required	17.8		21.9	
Thermal Energy Required	71.2		87.6	Assumes 25 % Thermal Efficiency

equivalent to 116 kg results in 10,162 $kW_{th}hr$/barrel of $(CH_2)_n$. However this estimate assumes 100 % conversion for the methanol and $(CH_2)_n$ processes. In actuality, typical methanol synthesis units have a 99.5 % conversion to methanol, while results of the Motuni, New Zealand MTG plant show a 97 % conversion to $(CH_2)_n$. Therefore the net overall thermal energy required is 10.5 $MW_{th}hr$/barrel of $(CH_2)_n$ or 10.5 MW_{th} for 1 barrel of $(CH_2)_n$ per hour. Note that this corresponds to a nominal energy from combustion of the $(CH_2)_n$ of 48.4 MJ/kg or 1.6 $MW_{th}hr$ per barrel of (CH_2). Thus the overall efficiency of conversion from nuclear thermal energy to jet fuel thermal energy is about 15 %. Also note that approximately 80 % of the energy input is required in the electrolytic production of hydrogen. Thus other process steps are inconsequential in terms of the overall energy balance; their requirements will impact mainly on space and weight requirements.

4.7 Summary

This chapter has presented the various individual processes required for the production of a naval synthetic fuel. Several sources for hydrogen and carbon dioxide were discussed, with seawater providing the best source for a naval application. Most importantly, this chapter established the energy requirements for such a synthetic fuel plant, which will be utilized in chapter 5 to size the subject naval application.

Chapter 5

NAVAL PLATFORM AND POWER PLANT INTEGRATION

5.1 Introduction

The integration of a synthetic fuel plant with a nuclear power plant is the sole premise of this work. This combination offers total energy independence and no net carbon dioxide emissions. For a naval application, the military advantages are substantial. This chapter will discuss three naval platform applications; a nuclear powered aircraft carrier (CVN), a barge, and an auxiliary ship such as a fleet oiler. The CVN application would be more limited, however, producing only fuel for the embarked aircraft. The barge application would be similar to other floating nuclear power plant (FNPP) designs, except that its production is synthetic fuel vice electricity. The mission of the auxiliary ship application is to produce fuel and deliver it to the aircraft carrier and other ships in the deployed fleet. Lastly, the use and benefits of a High Temperature Gas Cooled Reactor (HTGR) will be discussed and compared to the proposed PWR powered synthetic fuel plant.

5.2 Aircraft Carrier Based

The use of JP-5 is a function of the number and type of embarked aircraft and sortie (missions) rate. In addition to the nominal amount of flying per day, relevant to the threat level, additional sorties are flown as specific events occur, such as a strike, immediate air threat or an ASW (anti-submarine warfare) prosecution. For this examination, an estimate of the average JP-5 fuel consumption rate of 2500 gallons per sortie is assumed (C-7). A nominal carrier air wing has about 85 aircraft; in wartime, the

average sortie rate would probably be between one and two sorties per aircraft per day. Therefore a reasonable JP-5 consumption rate to assume is between 5,060 barrels (212,000 gallons) and 10,120 barrels (425,000 gallons) per day. Peacetime consumption would obviously be much lower and will be assumed to be half of the wartime rate or between 2,530 to 5,060 barrels per day.

The aviation fuel capacity for the Nimitz class carrier (includes all nuclear powered aircraft carriers except one) is reported as 9000 long tons (J-1). Assuming the density of JP-5 to be 800 kg/m^3 (50.0 lb/ft^3) yields a total capacity of approximately 72,000 barrels (~3 million gallons). Typically for damage control and stability concerns the liquid volume can never be less than 40 % of full volume. Therefore, operationally, the onboard availability of JP-5 is 60 % of capacity or 43,200 barrels. Using the above peacetime JP-5 consumption rates, with 43 to 85 sorties per day, the CVN must replenish aviation fuel every 8 to 17 days.

To properly examine the potential installation of a synthetic fuel plant onboard a CVN, the propulsion plant power must be known. Reference B-12 reports the main propulsion plant rated at 280,000 bhp (209 MW) and the electric plant rated at 64 MW for a total power of 273 MW. Although there are other steam loads in the propulsion plant, the main propulsion and electric plant are the major loads. Naval steam propulsion plants are simple Rankine cycles and have about a 25 % thermal efficiency. Therefore an equivalent of 273 MW output (electric and shaft) power gives a total thermal power of 1092 MW_{th} for a Nimitz class CVN.

The fundamental purpose of a nuclear power plant on a CVN is obviously for propulsion. However, Navy vessels typically do not operate at 100 % power for long periods of time. For a hypothetical conservative example, it is assumed that the total 64 MW_e is required for electrical demand, however, only 25 % of the available propulsion and catapulting steam power is needed (52 MW_e or 70,000 bhp). It is estimated that at this power level the CVN could still operate at approximately 15 knots or better. Therefore 157 MW_e could be exploited to power a synthetic fuel plant. From chapter 4 it was determined that it took 10.5 MW_{th} or 2.6 MW_e to produce 1 barrel of $(CH_2)_n$ per hour. With the available power, 60 barrels of fuel per hour or 1440 barrels per day could be produced. This is approximately 57 % of the assumed daily peacetime consumption rate (2,530 barrels per day with 43 sorties per day). Although it could augment the onboard supply, the production or makeup rate is not enough to fully augment the fuel inventory and outside sources (underway replenishment) would still eventually be required. Table 5.1 shows various consumption rates and the associated time until a limiting condition of 40 % JP-5 inventory results.

Table 5.1
Consumption Rates of JP-5 and Days Until Refueling is Required
(CVN with 1440 barrel per day synthetic fuel plant)

Barrels of JP-5 per day (Sorties per day)	**Days until 40 % of onboard JP-5 capacity is reached**
1785 (30)	125
2530 (43)	40
5060 (85)	12
10120 (170)	5

The dedicated power (157 MW_e) could temporarily restrict operations which require a fast and combat ready power source. Operation in this manner would also require much more frequent refueling of the onboard nuclear reactors (e.g.. approximately every five years vice approximately 20 years (S-18) due to sustained reactor operations near 100 % power). The alternative of increasing the rating of the reactor plant is also unattractive, since it would have to be roughly two times (80 %) more powerful to supply the total JP-5 usage for peacetime operations. Furthermore, as mentioned in chapter 4, the synthetic fuel plant requires electrical energy and therefore many more turbine generators (TGs) would be required. This requirement makes electric drive more attractive for a synthetic fuel plant CVN. The added TGs would require additional space, and could be installed in lieu of the four propulsion turbines and shafting associated with the current mechanical drive system. For these major reasons the use of a synthetic fuel plant onboard a CVN is not beneficial nor recommended for present day application.

5.3 Barge Based

The concept of locating the naval synthetic fuel plant on a barge is another possible alternative approach. The barge option, would in all likelihood only have the nuclear reactor plant(s) and synfuel plant on board. The added storage volume would be provided by other barges or by an oiler abreast the barge. Additionally, the barge synfuel plant should in principle be no more difficult (and arguably easier) than installing a similar plant on board a nuclear powered ship. Regardless, the installation of nuclear reactor plants on board waterborne barges or non-propelled vessels has been studied on a limited basis, but never fully tested. The Sturgis (MH-1A) Floating Nuclear Power Plant built for the U.S.

Army was a 10 MW_e plant mounted in a modified World War II era Liberty Class ship hull (B-13). It was a "marriage of convenience" based on an available ship hull and the desire for a rapidly produced power supply for isolated military posts and was therefore not optimized. Additionally, there were four conceptual barge studies conducted that are useful to examine; the Atlantic Generating Station (AGS), the Oak Ridge National Laboratory (ORNL) barge, the Russian nuclear floating desalination plant APVS-40, and the Russian nuclear floating power plant PAES-100. These floating nuclear power plants (FNPPs) have many aspects in common with the proposed synfuel barge.

The AGS was to be a "first of a kind" floating nuclear power plant, which would be constructed in Florida, then towed to and operated within a man-made breakwater just off the New Jersey coast. This plant design was to be a standardized design, constructed under a manufacturing license and operated under a separate plant license at the site. The AGS is fully described in references N-5, U-1 and U-2. It was planned as a four loop PWR with a net capacity of 1150 MW_e (3425 MW_{th}). It was to be mounted and installed on a barge-like platform, as shown in Figs. 5.1 and 5.2. The barge dimensions were 122 m (400 ft) long, 115 m (378 ft) wide, and 12 m (40 ft) deep, which displaced approximately 160,000 Ltons when fully loaded in the operating mode. The expected draft was 10 m (32 ft). The barge was a grillage-type structure, compartmented into 60 sections of which 39 were watertight, producing a virtually unsinkable vessel (N-5). The longitudinal and transverse framing was designed to meet the requirements of the American Bureau of Shipping Rules for Building and Classing Steel Vessels and Barges.

The ORNL study investigated industrial energy alternatives to provide small

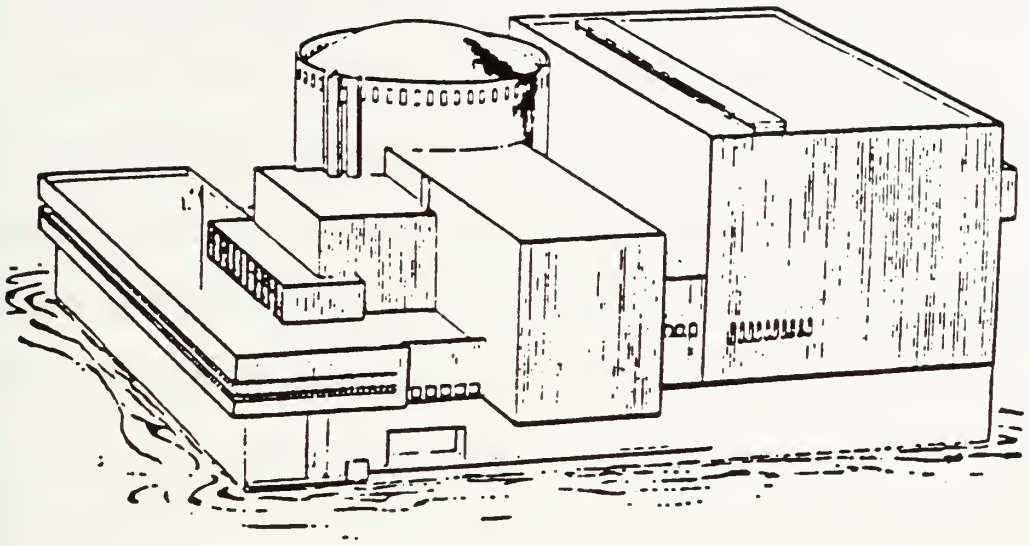


Figure 5.1
Side View of the Atlantic Generating Station
(Taken from reference N-5)

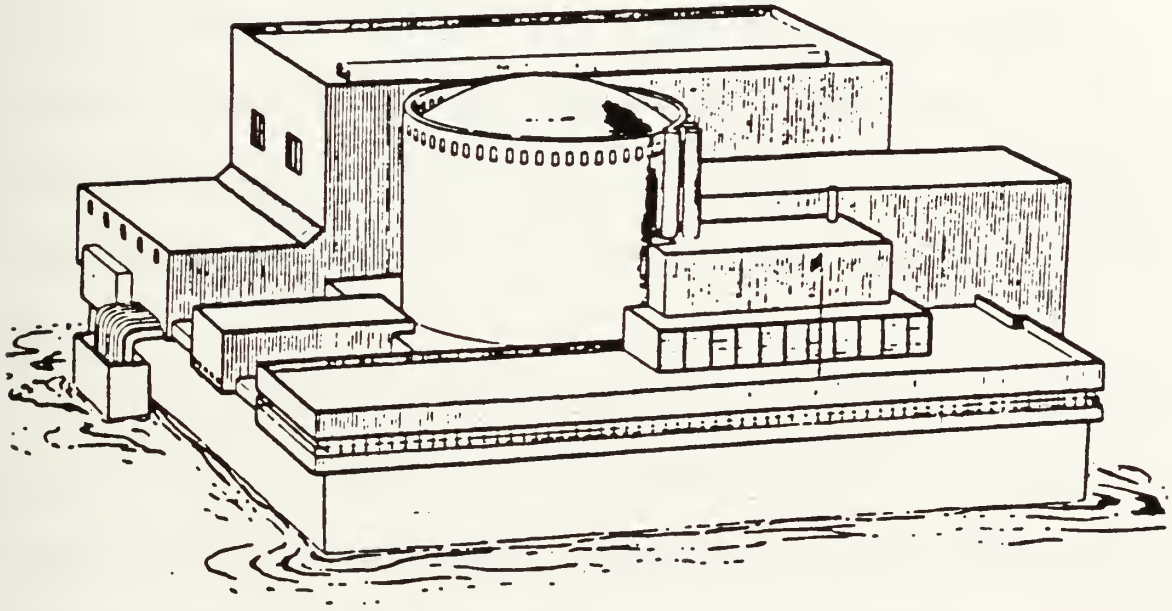


Figure 5.2
Front View of the Atlantic Generating Station
(Taken from reference N-5)

reactor plants for such industries as the paper, chemical, and petroleum refining industries (K-3). It used the 313 MW_{th} (91 MW_e) CNSG reactor plant developed by Babcock and Wilcox which was chosen for commercial ship propulsion (Savannah). It too was to be mounted and installed on a barge-like platform, as shown in Fig. 5.3. The barge dimensions were 98 m (320 ft) long, 32 m (105 ft) wide, and had a draft limited to 3 m (10 ft). Unlike other FNPPs, this study assumed the barge was only utilized to provide a means of transporting the power station to the site. Once transported it would be more permanently emplaced on a dry foundation or mooring system adjacent to the body of water. Therefore the barge displacement is not reported.

The APVS-40, shown in Figs. 5.4 and 5.5, is a special purpose non-propelled barge designed to produce drinkable water from seawater, via desalination (P-4). It uses one KLT-40 nuclear reactor plant (170 MW_{th}), the same plant which has successfully operated on board the Russian cargo carrier Sevmorput and various Russian icebreakers. The barge dimensions are 160 m (525 ft) long, 32 m (105 ft) wide, and 10 m (33 ft) deep which displaces approximately 28,500 Ltons when fully loaded. The expected draft is 6 m (20 ft).

Similar to the APVS-40, the PAES-100 barge can supply electric power to coastal industrial and remote areas difficult to access from land based plants (P-4). It is comprised of two KLT-40 nuclear reactor plants (340 MW_{th}). The barge dimensions are 120 m (394 ft) long, 30 m (98 ft) wide, and 10 m (33 ft) deep, which displaces approximately 20,000 Ltons when fully loaded. The expected draft is 6 m (20 ft). This conceptual design is very similar to that of the AGS.

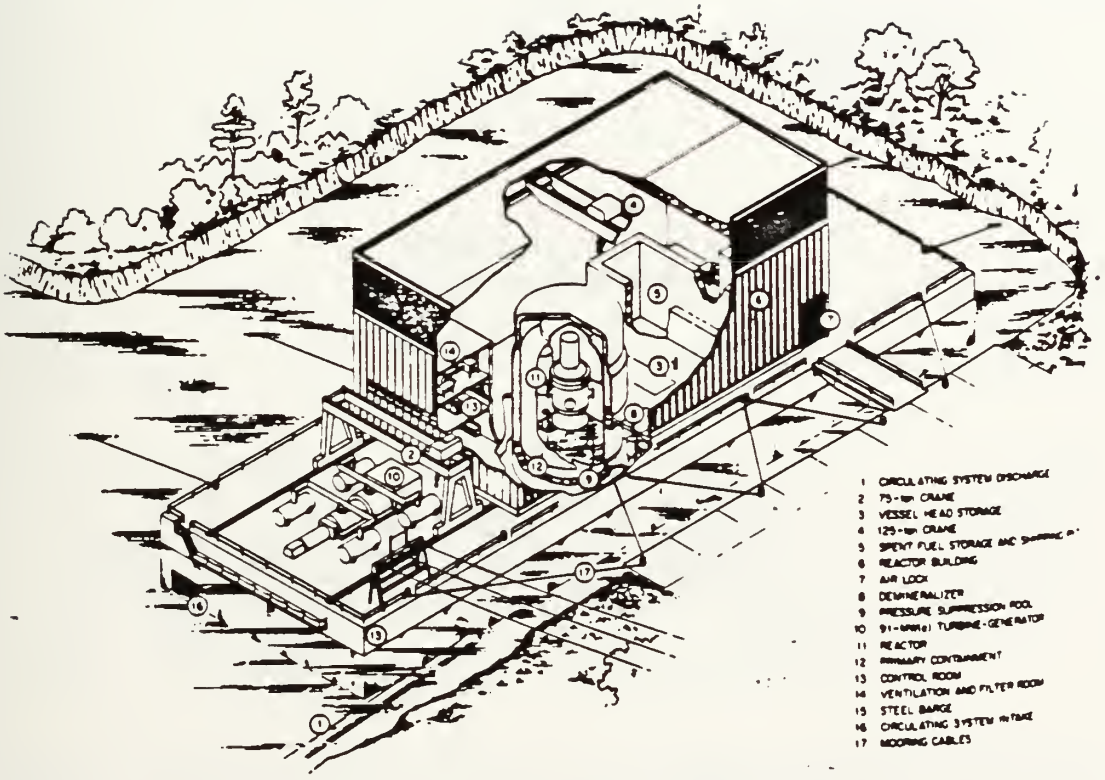


Figure 5.3
ORNL Platform/Barge
(Taken from reference K-3)

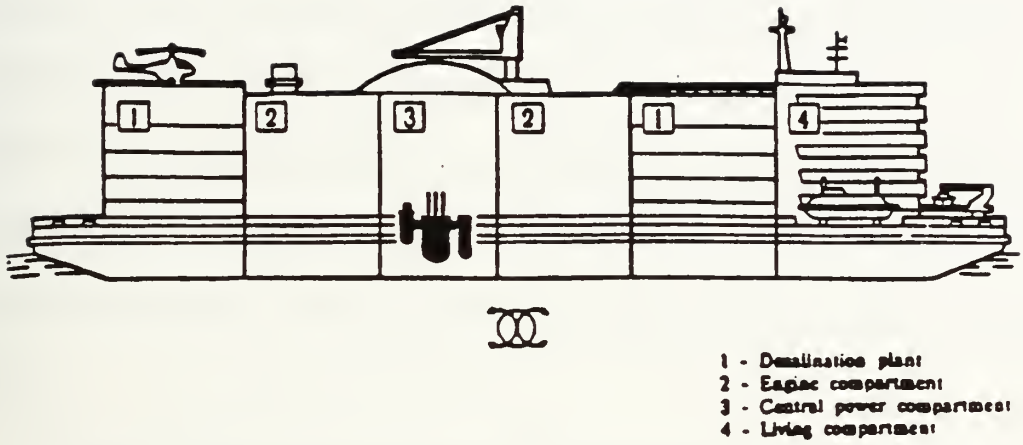
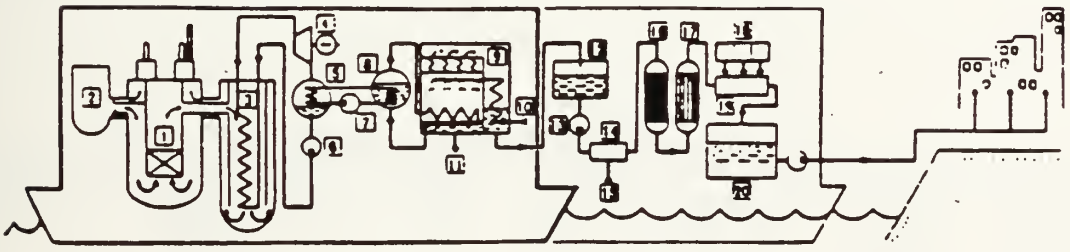


Figure 5.4
Ship Layout of APVS-40
(Taken from reference P-4)



1 — reactor; 2 — primary circuit circulator; 3 — steam generator; 4 — turbo-generator; 5 — condenser; 6 — secondary circuit electric pump; 7 — intermediate circuit electric pump; 8 — steam generator; 9 — distillation desalination plant; 10 — salt water; 11 — evaporated salt water; 12 — intaking tank for distillation; 13 — electric pump of the drinkable water preparation plant; 14 — mixer; 15 — H_2CO_3 solution; 16 — enrichment filter; 17 — running water sorbent containing filter; 18 — plant for fluorine, chlorine water treatment and stabilization; 19 — mixer; 20 — drinkable water tank.

Figure 5.5
Plant Flow Diagram for APVS-40
(Taken from reference P-4)

Another useful and somewhat relevant conceptual study was the 160 MW_e OTEC (Ocean Thermal Energy Conversion) Methanol Plantship discussed in reference A-1 and shown in Figs. 5.6 and 5.7. It was designed to use OTEC generated electrolytic hydrogen and oxygen, reacted with pulverized coal to produce methanol. The plantship was to be powered by sixteen 10 MW_e power modules grouped around two CWPs (cold water pipes). The methanol plant capacity was 1750 mt/day (15,000 barrels/day). The barge dimensions are 275 m (900 ft) long, 118 m (390 ft) wide, and 27 m (90 ft) deep, which displaces approximately 506,000 Ltons when fully loaded. The expected draft was 20 m (65 ft).

Table 5.2 summarizes the characteristics of the above conceptual plants. It is clear from this table that the OTEC methanol plant is much too large to be relevant to the present project. The excessive size is mostly due to the space requirements of the power modules and coal gasification plant; the methanol synthesis unit is estimated to only consume approximately 5 % of the topside area.

Table 5.2
Characteristics of Conceptual Barge Studies

Plant	Length (m)	Width (m)	Height (m)	Draft (m)	Displacement (Ltons)	Thermal Power (MW_{th})	Electric Power (MW_e)
AGS	122	115	12	10	160,000	3,425	1,150
ORNL	98	32	N/A	3	N/A	313	91
APVS-40	160	32	10	6	28,500	170	60
PAES-100	120	30	10	6	20,000	340	100
OTEC Methanol	275	118	27	20	506,000	480*	160

* reported as electric power (vice thermal power for others): hence multiplied by three to obtain a comparable value.

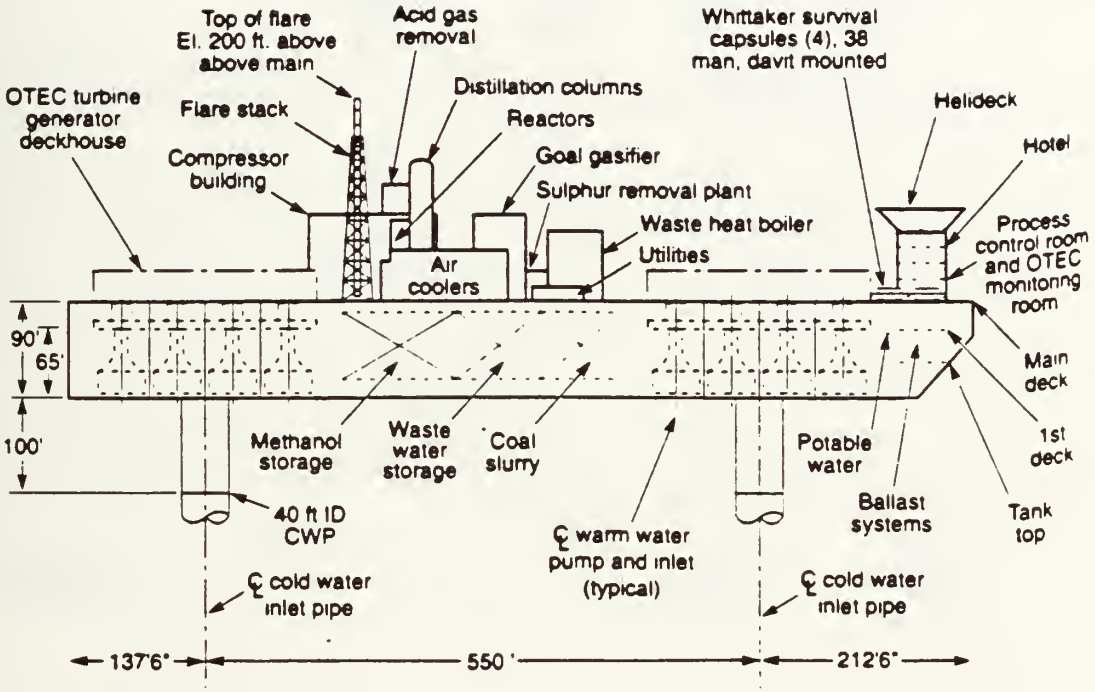


Figure 5.6
Profile of OTEC Methanol Plantship
(Taken from reference A-1)

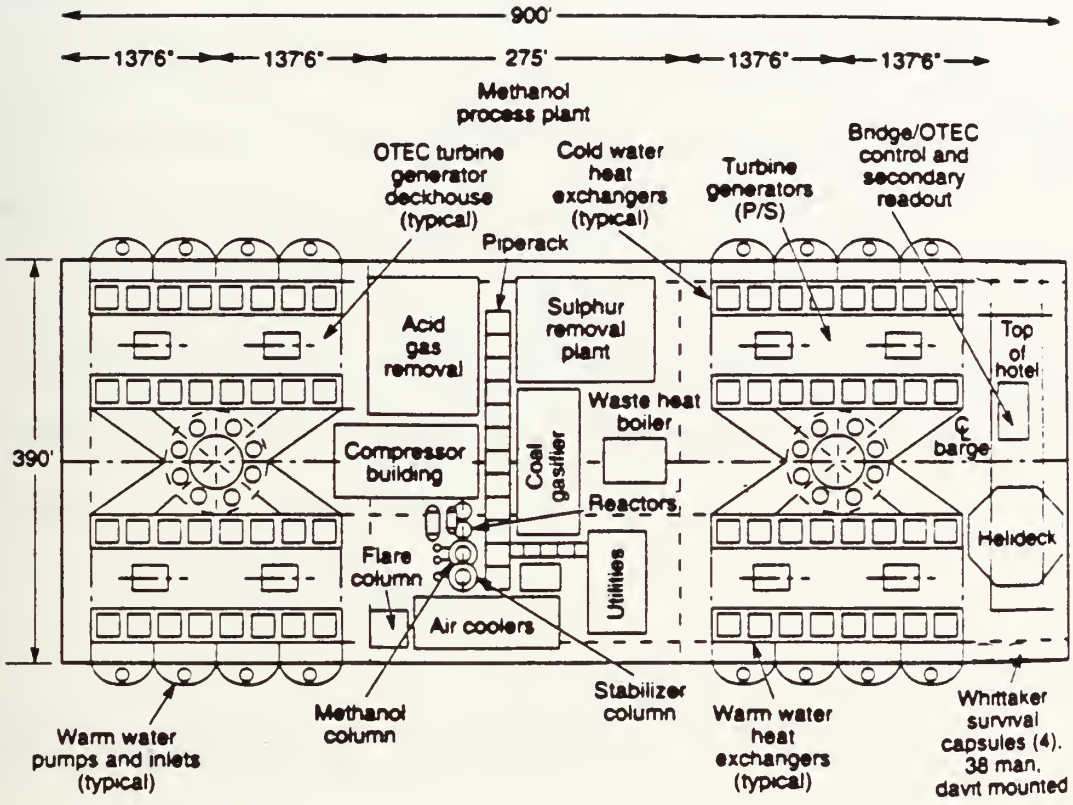


Figure 5.7
Top View of OTEC Methanol Plantship
(Taken from reference A-1)

To produce enough fuel for a CVN airwing, as described in section 5.2, would require a production rate of 2530 barrels per day assuming 43 sorties per day in a peacetime environment. Understandably, this is probably an overestimate since there are "no fly" days and other periods of inactivity, however, it is a conservative estimate in lieu of actual data. Therefore it requires approximately 1110 MW_{th} to meet this capacity, which is on the order of a Nimitz carrier power plant (2 reactor plants).

These prior studies provide information from which one can extract an approximate estimate of the size (displacement) of the platform (ship or barge) required to support the reactor and chemical processing plants for the task at hand.

Classical "economy-of-scale" considerations, based upon considerable experience in the chemical and electric power industries suggest that plant size increases at less than a 1:1 ratio with plant rating (i.e. output per unit time). A simple argument can be given in support of this observation, namely:

- capacity is proportional to volume, V
- cost and structural component weight is proportional to surface area, S

Then, for any geometric solid of fixed aspect ratio:

$$S \propto V^{\frac{2}{3}} \tag{5-1}$$

This suggests an economy-of-scale exponent of ~2/3; and indeed, as documented in reference P-10, the cost (roughly proportional to S) of many chemical plants scale with throughput at a power of ~0.7; the data base includes methanol synthesis plants and oil refineries.

Hence, lacking more detailed information, it will be assumed here that for our platform:

$$Displacement \propto Power^{\frac{2}{3}} \tag{5-2}$$

since, as shown in Chapter 4, the synfuel plant is dominated by the large electric power input needed to generate hydrogen by electrolysis. This approximation was tested against the available barge-mounted nuclear plant data and agrees within acceptable limits for this application. Therefore, since the power required (1110 MW_{th}) is about one third the capacity of the AGS (3425 MW_{th}), the approximate displacement or size would be 50 % of the AGS (or 80,000 Ltons). This crude estimate does not consider the weight of the synfuel plant, which however, is estimated to be a small percentage of the overall weight since the nuclear power plant has weight intensive components such as the radiation shielding, reactor vessel, turbine generators and pumps.

Using a similar argument, if a naval synfuel barge the size of the AGS is assumed, it could produce approximately 7830 barrels of fuel (either JP-5 or DFM) per day. Utilizing references S-19 and R-3, an average CVN battle group fuel consumption rate can be established. This "average" battle group consists of one CVN with embarked airwing, six gas turbine powered destroyer and cruiser escort ships, and an auxiliary oiler (AOE) to replenish the battle group. A scenario of 10 days at 20 knots transit phase, 20 days at 12 knots presence phase, and 50 days at 16 knots combat phase results in an average consumption rate of 4200 barrels per day of JP-5 and 4000 barrels per day of DFM (R-3). Therefore, the total power require to support combat fleet operations would

be roughly 3,600 MW_{th}: the same size as the AGS within the uncertainty of these estimates.

Some advantages and disadvantages of a barge mounted nuclear powered naval synthetic plant are shown in Table 5.3. Generally, like the CVN option, the use of a barge for the naval synthetic plant is not judged to be sufficiently beneficial, and is not recommended.

Table 5.3
Advantages and Disadvantages of a Barge Naval Synthetic Fuel Plant

Advantages	**Disadvantages**
1. Can utilize one large reactor plant (eg. 1100 MWe), hence economy of scale	1. Not fully mobile, difficult to move to forward deployed location
2. More easily constructed than an on-site terrestrial unit, especially for foreign bases	2. Must operate in open and clean water to avoid recycling carbon dioxide depleted seawater.
3. Also has commercial potential	3. Not as "seaworthy" as a ship
	4. More difficult to provide for reactor security, particularly in foreign port

5.4 Auxiliary Ship Based

The oiler option allows the co-location of the nuclear reactor plant, the synfuel plant, and the storage tanks, while also providing mobility of the fuel for supply to the fleet. For comparison purposes, a reference or standard oiler will be assumed. The "standard" defined here has an average displacement of 40,000 Ltons and is capable of storing 160,000 barrels of fuel oil. This was arrived at by analyzing the present day oilers, shown in Table 5.4, of the U.S. Navy. All, except the FLES, are operated routinely with

an operating naval fleet to refuel the battle group at sea. FLES (Fleet Logistics and Environmental Support Ship) was a recent conceptual design that is useful to show the displacement and tankage of a future replenishment oiler. The major reason for its reduced tankage capacity was the requirement of double hull construction.

Table 5.4
Oilers of the U.S. Navy (USS and USNS)

Class	Hull #	Displacement (Ltons)	Fuel Capacity (barrels)
Wichita	AOR-3	41,350	160,000
Henry J. Kaiser	T-AO 187	40,700	180,000
Cimarron	AO-177 Jumbo	37,870	180,000
Supply	AOE-6	48,800	156,000
Sacramento	AOE-1	51,400	177,000
FLES	N/A	40,000	107,000

Section 5.3 showed that a CVN carrier battle group required approximately 8200 barrels per day for the assumed scenario. This demand required about 3600 MW_{th} to power the synthetic fuel plant. The light load displacement of the Nimitz CVN is reported as approximately 73,000 Ltons (J-1). Utilizing the "2/3 rule" discussed in the previous section, and the Nimitz CVN displacement and power output, results in a required displacement of 161,700 Ltons. This is in very close agreement with the 165,400 Ltons found by a similar calculation using the AGS numbers. The weight of the synfuel plant is again assumed to be small compared to that of the nuclear power plant.

Thus in comparison with the standard fleet oiler, the nuclear synfuel ship must be a factor of four larger to supply the fuel needs of the deployed battle group. The weight of

the produced fuel only amounts to 1030 Ltons per day, which is also small in comparison. This proposed "nuclear fleet oiler" is very large by Navy standards but is comparable to a medium-sized crude carrier (MCC) or oil tanker. Commercial shipping uses the term deadweight tonnage (dwt), defined as the difference in displacement between loaded and unloaded conditions (i.e.. cargo load) while naval vessels are measured by total displacement (Ltons), either light or full load. Since an oil tanker's dwt is approximately 90% of its displacement, the terms dwt and displacement can in this case be considered equivalent. The MCC is defined as tankers up to 200,000 dwt (G-3). Therefore, a large "nuclear fleet oiler" based on a MCC hull form is a possible option and would probably be the most suitable application for a nuclear powered synthetic fuel ship. This ship would then be able to navigate to various locations with the fleet, and thereby avoid all the disadvantages listed in Table 5.3 for the barge-mounted synthetic fuel plant. Furthermore, although it is probably too large to be utilized for underway replenishment with combatants, it should be able to accommodate the standard fleet oiler alongside.

5.5 High Temperature Gas Cooled Reactors

Some predict that future naval nuclear power plants will be High Temperature Gas Cooled Reactors (HTGRs) since the Navy has almost 20 successful years of operating high efficiency modular gas turbines on ships and almost 30 years of nuclear power experience, thus a union of the two seems inevitable. It is not intended here to make a proposal or endorsement for a naval HTGR, but rather to outline the benefits to the proposed naval synthetic fuel plant if HTGRs come to fruition.

One leading proponent and manufacturer of HTGRs is General Atomics (GA), which is currently promoting a modular HTGR (MHTGR) plant using a gas turbine power cycle. They foresee the MHTGR as a multi-purpose reactor plant capable of providing energy, for not only synthetic fuel generation, but power generation, desalination, and steam generation for EOR (enhanced oil recovery) and district heating (M-8, M-9, M-10). GA's primary source for synthetic fuel is coal through a flame-free and thus emission-free coal gasification process. Flame-free gasification technology was tested during 1976 to 1984 on a pilot plant scale in Germany employing a immersion heat exchanger carrying heated helium to simulate the 15 MW_e AVR, Germany's prototype HTGR (G-4). Gasified coal can in turn be transformed into liquid fuel products such as methanol, jet fuel and gasoline. GA believes that with the abundance of U.S. coal reserves this technology has future commercial prospects.

HTGRs operate in the temperature region of 950 - 1150 ^{0}C (1740 - 2100 ^{0}F) and therefore besides achieving a higher thermal (Carnot or Brayton cycle) efficiency than a PWR, offer a temperature regime where thermo-chemical or high temperature steam electrolysis hydrogen production could occur. As noted in chapter 4, the well proven alkaline electrolysis process is responsible for approximately 80 % of the total energy requirement for the synfuel plant. Therefore, if the H_2 energy production "cost" could be reduced it would allow for a smaller nuclear plant for the same output capacity, or alternately a larger production rate for the same thermal output. The thermo-chemical process was briefly discussed in section 4.2.2 and ruled out mainly due to the desire to use existing PWR technology and the present lack of process experience. Likewise, high

temperature steam electrolysis, discussed briefly in section 4.2.1, was ruled out due to present material and fabrication difficulties. However, if in the future HTGRs are deployed , thermo-chemical cycles or high temperature steam electrolysis becomes more attractive. Reference Y-1 contains a review of the present state of nuclear hydrogen production capabilities. It lists over 70 thermo-chemical cycles that have been researched since the 1960's in the United States, Europe, former Soviet Union, and Japan. Some of these theoretical studies were tested on a bench/pilot plant scale and therefore only a few are thought to have practical applications.

Hydrogen production with conventional electrolysis was shown to required 70.5 $kWhr_{th}$/kg of $(CH_2)_n$, which includes a 80 % electrolyzer efficiency and 25 % PWR thermal efficiency. The initial projected theoretical efficiency for thermo-chemical cycles under investigation is near 50 % (Y-1). When compared to the standard present day alkaline electrolysis overall process efficiency of 20 %, the energy reduction is obvious. For example, with high temperature thermo-chemical H_2 production (assuming all other portions of the synfuel plant remain the same) the reduction in H_2 production energy would lower the total energy requirements by over 45 %. Furthermore, with an assumed thermal efficiency of 40 % for a HTGR nuclear plant, vice 25 % for the PWR, the overall energy reduction would be over 55 %. Thus, the advantages of both the higher temperatures and thermal efficiency makes the HTGR a highly desirable option to consider for powering a naval synthetic fuel plant.

5.6 Summary

This chapter has integrated the estimated energy requirements to produce synthetic JP-5 and DFM with the most likely platform or application to supply fuel to a deployed naval battle group. Three alternatives were investigated: a CVN installed synfuel plant to supply only the embarked airwing, a barge mounted synfuel plant to supply the entire battle group, and a large auxiliary ship (much like a commercial oil tanker), also to supply the entire battle group. Of the three, the later was shown to be the best option considering mission requirements and present day technology. The possible future use of HTGRs was also investigated briefly, and shown to greatly reduce the total energy requirements if thermo-chemical or steam electrolysis processes are used to produce hydrogen, and also because it has a higher plant thermal efficiency. Therefore it is concluded that a nuclear powered, either PWR or HTGR, naval synthetic fuel plant is technically possible, and offers potentially significant advantages by creating an energy self sufficient battle group.

Chapter 6

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

The eventual need to develop alternative liquid fuels, based on finite and depleting fossil fuel inventories is evident. The established use of nuclear power, both for maritime propulsion and commercial electrical generation, offers one approach to mitigate this eventual shortfall, since nuclear power can also serve as the power source for a liquid synthetic fuel plant. The proposed naval synthetic plant uses ubiquitous feedstocks of carbon dioxide (CO_2) and hydrogen (H_2), both contained in seawater: an overall process flow diagram is shown in Fig. 6.1. The suggested motivation for a naval synthetic fuel plant is predominantly to offer a naval task force or battle group added "energy independence" and "tactical freedom" while deployed far from the continental United States. Furthermore, like nuclear power itself, such application involves no net generation of CO_2 and is a completely "green" technology. On a terrestrial, larger scale basis, the benefits of no CO_2 emission could become extremely advantageous, particularly if current concerns with the greenhouse effect are validated.

It is this concern with global warming that has led to a recent intensification of research and development into CO_2 mitigating technologies, primarily for separating CO_2 from the flue gases of fossil fueled power plants. Also, the study of the oceans' uptake of CO_2 is paramount in understanding the complete CO_2 cycle. Some propose to use the oceans as a sink for CO_2 disposal from land-based sources; however it has been the focus of the present work to extract CO_2 from seawater and use it as the source for production

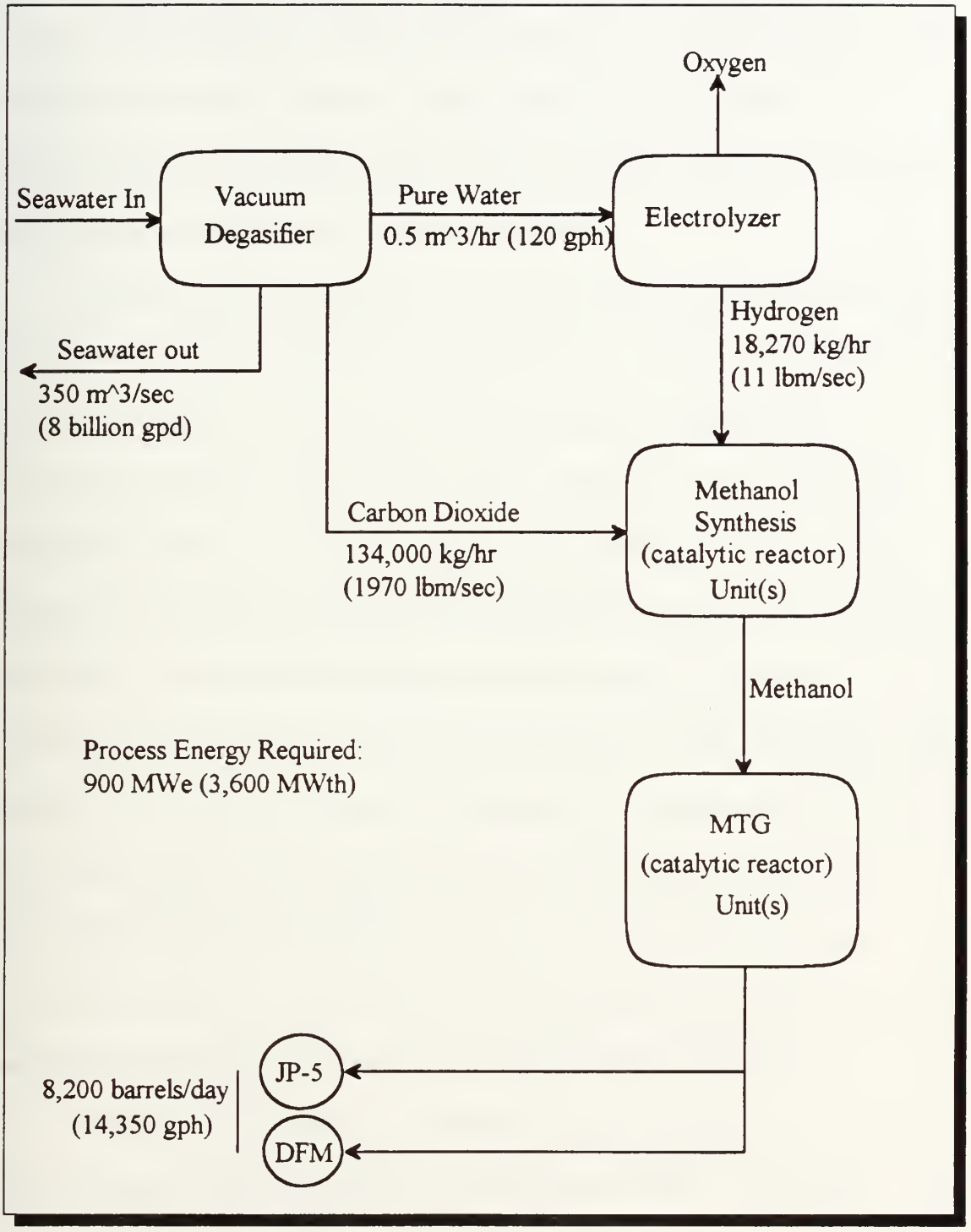


Figure 6.1
Overall Process Flow Diagram

of a hydrocarbon fuel. In addition to current CO_2 mitigating technologies, the last eight years of operating experience with the New Zealand MTG plant, sets a precedent for the naval synthetic fuel plant. This plant, utilizes natural gas and CO_2 as feedstocks to produce methanol, and the Mobil catalytic process to convert methanol to gasoline on a scale larger than required for the subject naval application.

Presently, the U.S. Navy uses JP-5 and DFM fuels for aircraft and ships. Thus for the near-term, the product of the naval synthetic fuel plant is JP-5 or DFM. Since these two fuels are similar in composition, they are equivalent for this analysis; only JP-5 is considered. Currently, to produce these products, methanol must be produced as an intermediate product. The direct use of methanol as a fuel for gas turbines and diesel engines can be regarded as a potential mid-term application with some minor changes in engine design. Many believe that methanol will be the energy vector of a new climate-neutral energy system (S-20) since it produces less CO_2 than current fuels. Lastly, the first step with both methanol and JP-5 production is producing hydrogen. Therefore, if or when hydrogen becomes a major fuel (commonly referred to as the hydrogen economy), the added steps of methanol and JP-5 conversion would not be required. These various pathways are shown in Fig. 6.2. Consequently, regardless of the desired naval fuel, a nuclear-based synthetic fuel plant can be utilized to produce it.

Presently, the preferred way to produce hydrogen on a large scale basis from non-hydrocarbon sources is via alkaline water electrolysis, which is a well proven technology. This process is the most energy intensive of all the processes used to produce

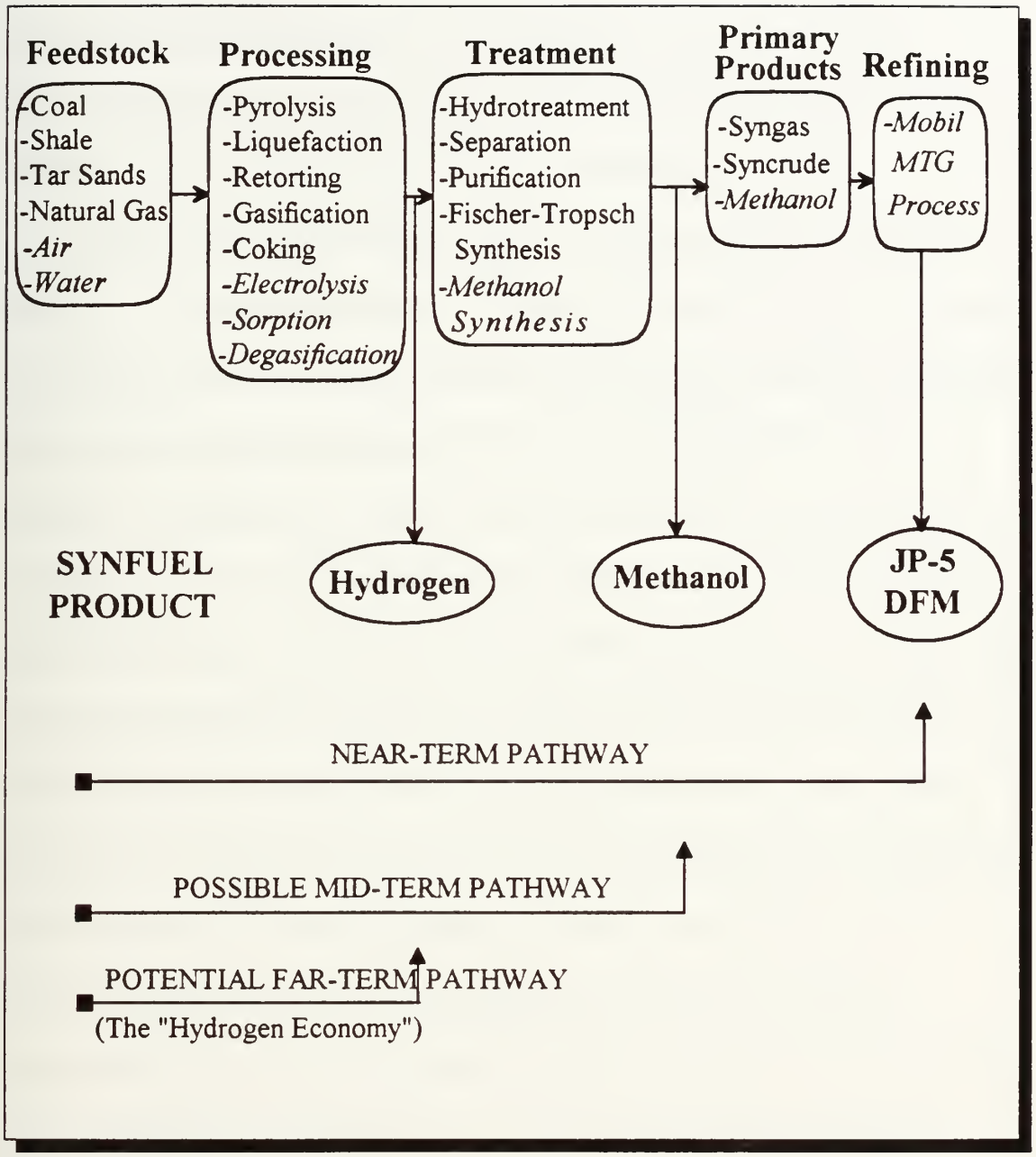


Figure 6.2
Pathways for Alternative Fuels

synthetic JP-5, and consumes approximately 80 % of the total input energy. Other methods to produce hydrogen, such as high temperature steam electrolysis and thermo-chemical processes, have limited if any practical experience presently but these technologies may eventually mature if HTGR's are utilized as the heat source.

Unlike electrolysis, the extraction of CO_2 from seawater is not as well known a technology. CO_2 is present in seawater (~100 ppm total, mostly as bicarbonate ion) and air (~350 ppm), and due to the density differences between these mediums, CO_2 extraction from seawater should require less energy and volume than an equivalently sized atmospheric stripping system. Previous studies (C-6 and S-8) recommended the scrubbing of atmospheric CO_2 for synthetic fuel production mainly so that it would also provide for terrestrial applications. CO_2 and other non-condensable gases are removed via degassing from condensate streams in power plants, as well as by producers of high purity water. Two present examples of gas removal from seawater are the direct contact condensers in the open-cycle ocean thermal energy conversion (OC-OTEC) system (Z-1, Z-2) and the vacuum deaeration of seawater for offshore oil platform seawater injection (H-11). However, these applications focus on O_2 removal; CO_2 extraction is currently a non-optimized process. A vacuum degasifier was shown to require a potentially tolerable energy expenditure for stripping CO_2 from seawater, and was therefore used for this analysis.

Once the CO_2 and H_2 are obtained they are combined in a heterogeneous catalyst reactor to produce methanol. Various manufacturers produce methanol synthesis plants for coal gasification and reforming of natural gas. Recently, technological development

has led to lower pressure methanol synthesis; Lurgi is marketing a unit specifically tailored to only CO_2 and H_2. The synthesis reaction is given by the following equation:

$$CO_{2(g)} + 3H_{2(g)} \Rightarrow CH_3OH_{(l)} + H_2O_{(g)} \qquad (6\text{-}1)$$

This is an exothermic reaction, and no thermal energy input is required from the nuclear reactor plant for this process.

Methanol as the intermediate product, is then converted by the MTG process to JP-5. Although the MTG process is currently utilized in New Zealand for gasoline production, it is indeed possible to alter the catalyst slightly and produce a liquid product similar to the composition of JP-5. For this analysis, it was assumed that JP-5 can be considered equivalent to $(CH_2)_n$. The MTG reaction is given by the following equation:

$$nCH_3OH_{(l)} \Rightarrow (CH_2)_{n_{(l)}} + nH_2O_{(g)} \qquad (6\text{-}2)$$

Like methanol synthesis, this reaction is also exothermic and the sum of the heat of vaporization of methanol and the sensible heat required to bring methanol to the reaction temperature balances the heat of reaction and no net energy input is required.

Table 6.1 shows the overall energy requirements for each individual process in the proposed naval synthetic fuel plant on a per kilogram of $(CH_2)_n$ basis. As seen, most of the energy is consumed in the form of electric energy. The thermal energy processes are the heatup of H_2 and CO_2 for methanol synthesis and the heatup of methanol for the MTG process. With proper process design and optimization, the resultant energy generation from methanol synthesis and MTG exothermic reactions can be utilized to provide all the thermal energy requirements (heatup). Thus there is no net thermal energy input. The

Table 6.1
Overall Energy Requirements

Process Step	Theoretical Energy (kWhr/kg of $(CH_2)_n$)	Efficiency of Process Step (%)	Predicted Process Energy (kWhr/kg of $(CH_2)_n$)	Notes
Electrolysis for H_2 generation	14.1	80	17.7	Section 4.2.4 (Electric)
CO_2 separation from seawater	1.7	90	1.9	Section 4.3.3 (Electric)
H_2 compression to 100 bar	1.6	90	1.8	Section 4.4.1 (Electric)
CO_2 compression to 100 bar	0.41	90	0.45	Section 4.4.1 (Electric)
H_2 heatup to 270 ^{0}C	0.37	N/A	0.37	Section 4.4.1 (Thermal)
CO_2 heatup to 270 ^{0}C	0.24	N/A	0.24	Section 4.4.1 (Thermal)
Methanol Synthesis	-1.7	N/A	-1.7	Section 4.4 (Thermal)
MTG	-0.9	N/A	-0.9	Section 4.5 (Thermal)
Total Electric Energy Required	17.8		21.9	
Thermal Energy Required	71.2		87.6	Assumes 25 % Thermal Efficiency

energy input in the form of electrical energy is assumed to be provided by a 25 % thermally efficient naval nuclear power plant, while the methanol synthesis and MTG conversion efficiencies are 99.5 % and 97 % respectfully. The net overall thermal energy required for this naval synthetic fuel plant was calculated to be 10.5 MW_{th}hr/barrel of JP-5. The overall efficiency of conversion from nuclear thermal energy to jet fuel thermal energy is approximately 15 %.

Based on this energy requirement it was then possible to size the nuclear synthetic fuel plant for specific naval applications. Three naval platforms were investigated; a nuclear powered aircraft carrier (CVN), a barge, and an auxiliary ship similar to a fleet oiler. The CVN option, with the present power rating, was not recommended because it could not fully produce enough fuel to support the airwing's usage requirements. Similarly, the barge option was not recommended mainly due to mobility constraints in a forward deployed location. It was determined that approximately 3,600 MW_{th} (900 MW_e) were needed to meet the needs of a deployed CVN carrier battle group, producing both JP-5 and DFM: approximately 8,200 barrels per day of fuel. The best platform therefore, is a large auxiliary ship, similar in size to a medium-sized crude oil carrier (MCC): i.e. oil tanker. It offers mobility, stability, a large volume for the nuclear and synthetic fuel plants, as well as ample storage volume. For comparison purposes, the power required is approximately a factor of three larger than a Nimitz class CVN.

6.2 Conclusions

Production of a liquid synthetic fuel, such as JP-5, is technically feasible for a naval application using well proven PWR nuclear plant technology to generate process

electricity. Although the economics of the proposed synthetic fuel plant were not seriously analyzed, an approximate production cost for JP-5 can be made. Of the total energy requirements to produce JP-5, about 80 % is due to water electrolysis. Assuming the net H_2 production cost for water electrolysis is \$22.63 per 100 m^3 (C-10), the cost for just H_2 production results in \$126 per barrel of JP-5 (or \$3.00/gallon). The actual cost of the MTG process (not including natural gas cost) from New Zealand data was \$45 per barrel in 1987 (first year of production) and estimated to be \$18 per barrel (\$0.43 per gallon) for 1996 after all loans are repaid (M-2). Therefore, it is the cost of hydrogen that is the limiting factor for the naval synthetic fuel plant. However it is difficult and speculative to compare commercial fuel cost (with no added externalities) to the fuel cost for a naval application. The benefits of having a battle group with "energy independence" and "tactical freedom" are difficult to quantify.

The recommended naval platform, the "nuclear fleet oiler," was calculated to produce 8,200 barrels of fuel per day which is 57 % of the capacity of the New Zealand Gas-to-Gasoline plant. Component dimensions and weights for the New Zealand plant are not available, however, the entire plant (including MTG and methanol synthesis units) was constructed in 76 preassemblies by Hitachi-Zosen Ltd. in Japan and shipped to New Zealand. At this point it appears reasonable to assume the naval synthetic fuel plant can be contained and carried on board the "nuclear fleet oiler".

While a large oil-tanker-size ship should be considered as the reference application, Navy analysts have also recently considered large sea-based platforms, such as floating islands and a very large aircraft carrier, both maintaining a minimum of a 2000 feet runway

(N-8). It is quite possible that a naval synthetic fuel plant could be associated with or installed within the sea-based platform, providing platform power and fuel for the deployed fleet.

The naval synthetic fuel plant, regardless of its ultimate installation requires a large amount of nuclear energy. Since the nuclear reactor operates at a considerably higher capacity (near 100 % power), the reactor core would require refueling more frequently than present ship propulsion reactors. In view of the current downsizing of the Navy, concerns exist with maintaining an adequate industrial base for naval construction and maintenance, particularly in regard to the highly trained nuclear work force. Reference B-14 discusses the costs involved with a shut down or a lower rate of production of nuclear submarines and the associated production gaps that would be created. Therefore, the construction of several "nuclear fleet oilers" with their associated frequent refuelings would enhance the capability of commercial and naval shipyards in maintaining nuclear production trade skills and proficiency, in an environment of reduced nuclear ship construction. This application could also be the precursor to later terrestrial applications if the greenhouse effect proves to have a significant detrimental impact.

Table 6.2 summarizes the major conclusions of this study.

Table 6.2
Major Conclusions for a Naval Synthetic Fuel Plant

1. Synthetic fuel production requires approximately 10.5 MW_{th} per barrel of fuel in the form of electric energy (~2.6 MW_e).
2. Hydrogen generation dominates the net energy requirements (~80 %).
3. A ship the size of a commercial oil tanker is required for a "nuclear fleet oiler" producing sufficient fuel supplies for a deployed carrier battle group.
4. The process for CO_2 extraction from seawater is not well proven and needs further research. Corrosive chemicals and excessive thermal energy should not be utilized for a naval application.
5. HTGR's, if utilized in the future, could be used to operate high temperature hydrogen processes (steam electrolysis or thermo-chemical) and thereby lower the total plant energy requirements.
6. Naval applications may lead to commercial applications which reduce net CO_2 emissions if utilized on a large scale basis.

6.3 Recommendations

On the basis of the analysis performed of a naval nuclear synthetic fuel plant, it is recommended that the following actions be taken to further develop the concepts and alternatives suggested within:

1. Perform a detailed experimental evaluation and optimization of CO_2 extraction from seawater utilizing vacuum deaerating technology. If CO_2 extraction from seawater is determined not to be practical, examine the alternative of absorption from air.

2. Carry out an in-depth cost and benefit analysis of a synthetic fuel supply system for U.S. Naval applications.

3. Evaluate whether HTGR technology offers any significant advantages for synthetic fuel production on board ships.

4. Pursue high temperature steam electrolysis, thermo-chemical, or other more efficient processes to reduce the energy requirements for hydrogen generation.

5. Perform a design study of a ship ("nuclear fleet oiler") suitable for the installation and operation of a naval synthetic fuel plant. Emphasis should be placed on load distribution, propulsion plant and electric drive systems, chemical plant layout, CO_2 from seawater extraction unit, underway replenishment capability and ensuring adequate storage volume to support fleet operations. Waterjet propulsion should also be evaluated based on the large volumetric flowrate of seawater required to provide CO_2. Additionally, the ease in refueling of the nuclear power plant(s) should be considered, since they will operate almost continuously at full power.

APPENDIX A

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APPENDIX B

LIST OF NUCLEAR POWERED MARINE VESSELS

This appendix is provided to serve as a concise and current listing of the world's nuclear powered marine vessels since no other reference was readily available and because such precedent is relevant to the proposed use of shipborne reactors in the application examined in the present thesis. It was derived from information found in references B-4, J-1, P-1, O-1, O-2, and O-3. It is interesting to note that in terms of plant experience, the marine application of pressurized water reactors (PWRs) for ship propulsion and electrical generation greatly surpasses the commercial nuclear power electrical generation industry. Worldwide maritime PWR installations to date total 762 units, including commissioned and decommissioned vessels. This compares to 490 units for commercial nuclear power reactors (including all reactor types; Pressurized LWRs, Boiling LWRs, Gas-cooled reactors, Heavy water reactors, Graphite moderated LWRs, and Liquid-metal cooled fast-breeder reactors) both in-service and out-of-service to date (N-1). Of the 490 units, 284 are PWRs, which is about 37 % of the total PWRs used in marine applications. Table 1 summarizes the listing on a by-country basis.

Table B.1
Number of Marine PWR's by Country

Country	# of Marine PWR's
C.I.S. (formerly Soviet Union)	482
United States	227
United Kingdom	27
France	17
China	7
Germany	1
Japan	1
Total	762

UNITED STATES — TOTAL 227

Submarines	Hull Number
Ohio Class (1 PWR each)	
Ohio	726
Michigan	727
Florida	728
Georgia	729
Henry M.Jackson	730
Alabama	731
Alaska	732
Nevada	733
Tennessee	734
Pennsylvania	735
West Virginia	736
Kentucky	737
Maryland	738
Nebraska	739
Rhode Island	740
Maine	741
Lafayette Class (1 PWR each)	
Lafayette	616
Alexander Hamilton	617
Andrew Jackson	619
John Adams	620
James Monroe	622
Nathan Hale	623
Woodrow Wilson	624
Henry Clay	625
Daniel Webster	626
James Madison	627
Tecumseh	628
Daniel Boone	629
John C. Calhoun	630
Ulysses S. Grant	631
Von Steuben	632
Casimir Pulaski	633
Stonewall Jackson	634
Sam Rayburn	635
Nathaniel Greene	636
Benjamin Franklin	640
Simon Bolivar	641
Kamehameha	642
George Bancroft	643
Lewis and Clark	644
James K. Polk	645
George C. Marshall	654
Henry L. Stimson	655
George Washington Carver	656
Francis Scott Key	657
Mariano G. Vallejo	658
Will Rogers	659
Ethan Allen Class (1 PWR each)	
Ethan Allen	608
Sam Houston	609
Thomas A. Edison	610
John Marshall	611
Thomas Jefferson	618
George Washington Class (1 PWR each)	
George Washington	598
Patrick Henry	599
Theodore Roosevelt	600
Robert E. Lee	601
Abraham Lincoln	602

Los Angeles Class (1 PWR each)

Los Angeles	688
Baton Rouge	689
Philadelphia	690
Memphis	691
Omaha	692
Cincinnati	693
Groton	694
Birmingham	695
New York City	696
Indianapolis	697
Bremerton	698
Jacksonville	699
Dallas	700
La Jolla	701
Phoenix	702
Boston	703
Baltimore	704
City Of Corpus Christi	705
Albuquerque	706
Portsmouth	707
Minneapolis-Saint Paul	708
Hyman G. Rickover	709
Augusta	710
San Francisco	711
Atlanta	712
Houston	713
Norfolk	714
Buffalo	715
Salt Lake City	716
Olympia	717
Honolulu	718
Providence	719
Pittsburgh	720
Chicago	721
Key West	722
Oklahoma City	723
Louisville	724
Helena	725
Newport News	750
San Juan	751
Pasadena	752
Albany	753
Topeka	754
Miami	755
Scranton	756
Alexandria	757
Asheville	758
Jefferson City	759
Annapolis	760
Springfield	761
Columbus	762
Santa Fe	763
Boise	764
Montpelier	765
Charlotte	766
Hampton	767
Hartford	768
Toledo	769
Tucson	770

Quiet Design (1 PWR each)

Glenard P. Lipscomb	685

Narwhal Class (1 PWR each)

Narwhal	671

Sturgeon Class (1 PWR each)

Sturgeon	637
Whale	638
Tautog	639
Grayling	646
Pogy	647
Aspro	648
Sunfish	649
Pargo	650
Queenfish	651
Puffer	652
Ray	653
Sandlance	660
Lapon	661
Gurnard	662
Hammerhead	663
Sea Devil	664
Guitarro	665
Hawkbill	666
Bergall	667
Spadefish	668
Seahorse	669
Finback	670
Pintado	672
Flying Fish	673
Trepang	674
Bluefish	675
Billfish	676
Drum	677
Archerfish	678
Silversides	679
William H. Bates	680
Batfish	681
Tunny	682
Parche	683
Cavalla	684
Mendel Rivers	685
Richard B. Russell	687

Permit Class (1 PWR each)

Permit	594
Plunger	595
Barb	596
Pollack	603
Haddo	604
Jack	605
Tinosa	606
Dace	607
Guardfish	612
Flasher	613
Greenling	614
Gato	615
Haddock	621

Tullibee Class (1 PWR each)

Tullibee	597

Skipjack Class (1 PWR each)

Skipjack	585
Scamp	588
Scorpion	589
Sculpin	590
Shark	591
Snook	592
Thresher	593

Halibut Class (1 PWR each)

Halibut	587

Triton Class (2 PWRs each)

Triton	586

Skate Class (1 PWR each)

Skate	578
Swordfish	579
Sargo	583
Seadragon	584

Seawolf Class (1 PWR each)

Seawolf	575

Nautilus Class (1 PWR each)

Nautilus	571

NR-1 Class (1 PWR each)

NR-1

Surface Naval Ships	Hull Number	Surface Commercial Ship
Enterprise Class (8 PWRs each)		NS Savannah (1 PWR)
Enterprise	65	
Nimitz Class (2 PWRs each)		
Nimitz	68	
Dwight D. Eisenhower	69	
Carl Vinson	70	
Theodore Roosevelt	71	
Abraham Lincoln	72	
George Washington	73	
John C. Stennis	74	
Long Beach Class (2 PWRs each)		
Long Beach	9	
Bainbridge Class (2 PWRs each)		
Bainbridge	25	
Truxton Class (2 PWRs each)		
Truxton	35	
California Class (2 PWRs each)		
California	36	
South Carolina	37	
Virginia Class (2 PWRs each)		
Virginia	38	
Texas	39	
Mississippi	40	
Arkansas	41	

RUSSIA

TOTAL 482

Submarines

	# in Class
Akula Class (2 PWRs each)	
Bars	
Leopard	
Pantera	
Puma	
Volk	
Tigr	
Charlie I Class(1 PWR each)	
unknown names	12
Charlie II Class (1 PWR each)	
unknown names	6
Delta I Class (2 PWRs each)	
Murena	19
Delta II Class (2 PWRs each)	
Murena-M	4
Delta III Class (2 PWRs each)	
Kalmar Class	14
Delta IV Class (2 PWRs each)	
Delfin Class	7
Echo I Class (2 PWR each)	
unknown names	5
Echo II Class (2 PWR each)	
unknown names	29
Hotel II Class (2 PWRs each)	
unknown names	8
Hotel III Class (2 PWR each)	
unknown names	1
November Class (2 PWR each)	
unknown names	15

	# in class
Oscar I Class (2 PWRs each)	
Granit Class	2
Oscar II Class (2 PWRs each)	
Antyey Class	10
Papa Class (2 PWR each)	
unknown names	1
Sierra I Class (2 PWRs each)	
Barracuda I Class	2
Sierra II Class (2 PWRs each)	
Barracuda II Class	2
Typhoon Class (2 PWRs each)	
unknown names	6
Uniform Class (1 PWR each)	
Uniform Class	2
Victor I Class (2 PWRs each)	
unknown names	16
Victor II Class (2 PWRs each)	
Kefal II Class	7
Victor III Class (2 PWRs each)	
Kefal III Class	26
Yankee I/II Class (2 PWRs each)	
unknown names	34

Surface Naval Ships

Kirov Class (2 PWRs each)
Admiral Ushakov (ex-Kirov)
Admiral Lazarev (ex-Frunze)
Admiral Nakhimov (ex-Kalinin)
Pyotr Velikiy (ex-Yuri Andropov)

Ice Breakers

Lenin Class (3 PWRs)
Lenin

Ivan Moskvitin Class (2 PWRs each)
Ivan Moskvitin
Semyon Deshnev

Arktika Class (2 PWRs each)
Arktika (ex-Leonid Brezhnyev)
Leonid Brezhnyev (ex-Arktika)
Sibir
Rossiya
Sovetskiy Soyuz
Yamal (ex-Oktyabryskaya Revolutsiya)
Ural

Tamyr Class (2 PWRs each)
Tamyr
Vaygach

Surface Commercial Ships

Sevmorput (1 PWR)

Not Included in Total	# in class
Alfa Class (1 LMR each)	
unknown names	6
Mike Class (2 LMRs each)	
unknown names	1

FRANCE

TOTAL 17

Submarines	Hull Number
Le Redoutable Class (1 PWR each)	
Le Redoutable	611
Le Terrible	612
Le Foudroyant	610
L'Indomptable	613
Le Tonnant	614
L'Inflexible	615
Le Triomphant Class (1 PWR each)	
Le Triomphant	616
Le Temeraire	617
Le Vigilant	618
Rubis Class (1 PWR each)	
Rubis (ex-Provence)	601
Saphir (ex-Bretagne)	602
Casabianca (ex-Bourgogre)	603
Emeraude	604
Amethyste	605
Perle	606

Surface Naval Ships	Hull Number
Charles De Gaulle Class (2 PWRs each)	
Charles De Gaulle	91

UNITED KINGDOM TOTAL 27

Submarines	Hull Number
Resolution Class (1 PWR each)	
Renown	26
Repulse	23
Resolution	22
Revenge	27
Valiant Class (1 PWR each)	
Valiant	102
Warspite	103
Churchill Class (1 PWR each)	
Churchill	46
Conqueror	105/48
Courageous	50
Swiftsure Class (1 PWR each)	
Swiftsure	126
Sovereign	108
Superb	109
Sceptre	104/110
Spartan	105/111
Splendid (ex-Severn)	106/112
Dreadnought Class (1 PWR each)	
Dreadnought	101
Vanguard Class (1 PWR each)	
Vanguard	28
Victorious	29
Vigilant	30
Valiant	31
Trafalgar Class (1 PWR each)	
Trafalgar	107
Turbulent	87/110
Tireless	88/117
Torbay	90/118
Trenchant	91
Talent	92
Triumph	93

CHINA — TOTAL 7

Submarines	Hull Number
XIA Class (1 PWR each)	
XIA	406
unknown (lost in accident)	407
Han Class (1 PWR each)	
unknown	401
unknown	402
unknown	403
unknown	404
unknown	405

GERMANY — TOTAL 1

Surface Commercial Ships

Otto Hahn

JAPAN — TOTAL 1

Surface Commercial Ships

Mutsu

APPENDIX C

COMPOSITION AND PROPERTIES OF JP-5

The fuel used primarily for aircraft propulsion in the U.S. Navy is JP-5. JP-5 can also serve as a substitute ship propulsion fuel for conventionally powered ships. The particular specification for JP-5 is dictated by military specification (MILSPEC) MIL-T-5624. JP-5 is a broad based kerosene (reference H-1). Reference S-1 states that "tailored" kerosene's like JP-5 are also called Avcat fuel. Furthermore, it states that aviation fuels like JP-5 can contain several hundred different hydrocarbons. However, these various hydrocarbons can be grouped into four representative categories or families as shown in Table C.1.

Table C.1
Typical Hydrocarbon Composition of JP-5 (Avcat)

Paraffins	26%
Naphthenes	50%
Aromatics	22%
Olefins	2%

The usual formula employed in estimating the heat of combustion in Btu/lb for coal is the Dulong formula given by (B-1):

$$\Delta H_{Combustion} = 14544F_C + 62028\left(F_{H_2} - \tfrac{1}{8}F_{O_2}\right) + 4050F_S \text{ Btu/lb} \qquad \text{(C.1)}$$

where: F_C = fraction of carbon
F_{H2} = fraction of hydrogen
F_{O2} = fraction of oxygen
F_S = fraction of sulfur

Converting into conventional SI units (kJ/kg) and deleting the sulfur term (a negligible constituent for fuels of current interest), yields a modified SI Dulong formula:

$$\Delta H_{Combustion} = 33829.34F_C + 144277.13F_{H_2} - 18034.64F_{O_2} \text{kJ/kg} \qquad \text{(C.2)}$$

Table C.2 contains several hydrocarbons from the four families of hydrocarbons commonly present in transportation fuels. Using the composition of JP-5 given in Table C.1, the coefficients of the modified Dulong prescription were adjusted to minimize the difference between the actual and the empirical heat of combustion for a mix approximating JP-5. A modified JP-5 Dulong formula can therefore be derived for liquid fuels, and is found to be:

$$\Delta H_{Combustion} = 32786.28F_C + 141582.64F_{H_2} - 16537.58F_{O_2} \text{ kJ/kg} \qquad \text{(C.3)}$$

Selected hydrocarbons with actual and calculated heat of combustion values are shown in Table C.2. Note that differences in the physical state of the hydrocarbon, (i.e. liquid or gas) have not been taken into account in the preceding analysis.

Alternatively, the heat of combustion can be estimated by summing the average bond energies for each of the bonds of the individual compounds. Average bond energies are usually determined and tabulated for gaseous molecules. When reactants or products are liquids or solids, the enthalpies of vaporization or sublimation must be added to the calculated bond energies in the vapor phase to be valid. Similarly, approximations can be made for estimating the heat of formation. If the bond energy approximation technique is

utilized the results should be within +/- 10 % of the experimental values (E-1). For example, using the bond energy table, the heat of formation for methanol gas at 25 ^{0}C was calculated to be -52.2 kcal/mole which is within 8.5 % of the tabulated value of -48.1 kcal/mole. The use of a bond energy table is therefore important to determine the approximate energy content when the heat of formation or heat of combustion has not been experimentally determined. In practice the most common method to determine the heat of formation for a combustion fuel is to use its heat of combustion and subtract the heat of formation of the individual products (i.e. CO_2 and H_2O).

Reference C-1 lists the typical heat of combustion of JP-5 as 43,050 kJ/kg (18,500 Btu/lb) and a minimum specification of 42,600 kJ/kg (18,300 Btu/lb). The analysis of Avcat given in reference S-1, predicted the chemical composition as $CH_{1.83}$ while reference B-2 assumed the chemical composition of JP-5 as $CH_{1.94}$. Commercial jet fuel, which is typically less volatile than JP-5, has a chemical formula of $C_{10-15}H_{22-32}$ (V-1). However, for the purposes of this study, the chemical formula for JP-5 will be assumed to be $(CH_2)_n$, with n being the number of CH_2 groups in the molecule. Since the modified JP-5 Dulong formula predicts the heat of combustion fairly well, as shown by Table C.2, it is used to determine the heat of combustion for JP-5 in the energy balance required in the present work. The heat of combustion for CH_2 is calculated as 48,410 kJ/kg. Utilizing this calculated heat of combustion, the heat of formation can then be determined as described above. The heat of formation for CH_2 is calculated as -2,998 kJ/kg. For comparison with a typical $(CH_2)_n$ compound, the tabulated heat of formation for $C_{10}H_{22}$ (n-decane), in liquid form, is -2,118 kJ/kg. The difference between these two values predominately results

from the fact that the heat of formation calculated in this manner is the difference between two large numbers with their associated uncertainties. Table C.3 summarizes the results of the three suggested chemical formulas for JP-5; the differences are negligible and hence the use of the simpler version, $(CH_2)_n$, in formulating chemical reaction equations is acceptable. In conclusion, the practical JP-5 formula, is convenient and sufficiently accurate to use for our scoping analysis.

Table C.2.
Modified JP-5 Dulong Formula Results

Family	Fuel	Formula	delta H_{comb} (kJ/kg) Measured	delta H_{comb} (kJ/kg) Calculated	% Difference
Paraffin	*Methane (g)	CH_4	55,542	60,137	8.27
	*Ethane (g)	C_2H_6	51,907	54,666	5.31
	*Propane (g)	C_3H_8	50,371	52,676	4.58
	n-Octane (l)	C_8H_{18}	47,746	50,066	4.86
Naphthene	*Cyclopentane (l)	C_5H_{10}	46,957	48,424	3.13
	*Cyclohexane (l)	C_6H_{12}	46,607	48,422	3.89
	*Cycloheptane (l)	C_7H_{14}	46,864	48,420	3.32
Aromatic	*Benzene (l)	C_6H_6	41,860	41,211	-1.55
	Toluene (l)	C_7H_8	42,449	42,307	-0.33
	meta-Xylene (l)	C_8H_{10}	42,920	43,114	0.45
	Ethylbenzene (l)	C_8H_{10}	43,031	43,114	0.19
Olefin	*1-Butene (l)	C_4H_8	48,517	48,419	-0.2
	Propylene (g)	C_3H_6	48,772	48,422	-0.72
	1-Pentene (l)	C_5H_{10}	47,963	48,424	0.96
	*Ethylene (g)	C_2H_4	50,335	48,428	-3.79
	Carbon (s)	C	32,813	32,786	-0.08
	Hydrogen (g)	H_2	142,068	141,583	-0.34
	*Methanol (l)	CH_3OH	22,690	21,848	-3.71
	*Ethanol (l)	C_2H_5OH	29,688	29,937	0.84
	*Propanol (l)	C_3H_7OH	33,630	34,250	1.84

Notes:

1. The measured heat of combustion is given in kJ/kg when combustion takes place at atmospheric pressure and at either 20°C or 25°C with stoichiometric oxygen. An asterisk indicates combustion at 25°C, while no asterisk indicates 20°C. Therefore, since the Dulong formula is insensitive to temperature, the difference between 20°C and 25°C leads to a minor error.

2. Tables of combustion measurements are often reproduced with the opposite sign convention so that heats of combustion are listed as positive quantities.

Table C.3.
Composition and Heat of Combustion of Avcat, Theoretical and Practical JP-5

	Formula	% H_2	% C	delta $H_{Combustion}$ (kJ/kg)	delta $H_{Formation}$ (kJ/kg)
Avcat	$CH_{1.83}$	13.3	86.7	47,254	-2,814
Theoretical JP-5	$CH_{1.94}$	14	86	48,005	-2,941
Practical JP-5	CH_2	14.4	85.6	48,410	-2,998
Actual JP-5 (typical value)				~43,050 LHV* (~46,175 HHV)*	

Note:
*1. The disparity between the actual JP-5 heat of combustion and the others reported is mainly due to the heat of vaporization of water (2,420 kJ/kg). The actual JP-5 heat of combustion of 43,050 kJ/kg is the fuel's lower heating value (LHV). LHV is sometimes referred to as the net heat of combustion. When the water vapor product from combustion is condensed to liquid it is referred to as the fuel's higher heating value (HHV). Therefore, the hydrogen content of the fuel determines the amount of water vapor produced and hence the difference between HHV and LHV of the fuel. The Avcat, theoretical and practical JP-5 heats of combustion were all predicted by the modified Dulong equation and measure the HHV of the fuel. Other minor differences between the actual and predicted JP-5 heat of combustion values are due to the assumptions associated with the modified Dulong formula as shown by the minor differences in Table C.2.

2. In practice combustion is carried out in the presence of nitrogen (i.e. air) and non-stoichiometric (i.e. excess) oxygen. In addition, the combustion products plus residual N_2 and O_2 remain at high temperature.

APPENDIX D

SEPARATION OF CARBON DIOXIDE FROM SEAWATER

This appendix contains calculations for determining the energy requirement to separate CO_2 from seawater. Three separate processes are investigated, a single effect evaporator, a conventional vapor compression evaporator, and a modified vapor compression degassing tower. There are no commercial system designs or processes known to selectively remove CO_2 from seawater; however, the generic processes to deaerate or degasify liquids are found in many industrial applications. Degassing of water which generally contains dissolved gases, such as, air and carbon dioxide is an important feature in evaporators, degasifiers and condensers. In these components, when the liquid is at or above the boiling point most, if not all, of the gases are stripped from the liquid by the coexisting vapor phase. The terms "evaporators" and "degasifiers" are used here interchangeably: they differ mainly in whether the emphasis is on producing pure vapor from the liquid being evaporated or on removing non-condensable gases from the liquid. The volume of seawater required for CO_2 extraction and the associated volume of pure water required for hydrogen production are also estimated.

D.1 Single Effect Evaporator

The single effect evaporator, shown in Fig. D.1, is similar to a simple desalination unit to produce fresh water. Alternatively, it can be considered fundamentally similar to a low pressure feed heater or deaerating feed tank (DFT) used in many steam plants to deaerate and remove the non-condensable gases from the condensate. Regardless, the

approach here is to heat the incoming CO_2 laden seawater to a boiling condition to cause CO_2, water vapor and air to be liberated.

Extracting 1 kg/sec of CO_2 from seawater requires 10,000 kg/sec seawater feed (assuming seawater contains 100 ppm of CO_2). Assuming an inlet seawater temperature of 15 ^{0}C (59 ^{0}F), a bulk temperature in the evaporator of 100 ^{0}C (212 ^{0}F) would require 3600 MW_{th} per 1 kg/sec of CO_2 or 1000 kwhr/kg (~1.5 million Btu/lb) of CO_2. Clearly this is prohibitive. The pump work is neglected since it is only a small percentage of the required thermal energy. A multiple-effect evaporator could be used to reduce the energy input, however, this is still impractical since the energy requirement is orders of magnitude larger than desired. For example, to reduce the energy requirement to 1 kWhr/kg of CO_2 would require approximately 1000 stages, which is not feasible: multiple-effect evaporators typically have only 4 -5 stages. Alternatively, a regenerative heat exchanger (RHX) could be used to reduce the net temperature differential from 85 ^{0}C to about 20 ^{0}C; however that only reduces the thermal energy by a factor of four, which is still too energy intensive. Therefore heating the incoming seawater to liberate CO_2 is not an option for this application.

D.2 Conventional Vapor Compression Evaporator

Vapor compression evaporators (stills) are designed to recycle the latent heat of vaporization of the produced steam. Vapor compression is typically used when cheap mechanical energy is readily available and the evaporator can operate with a small temperature differential, such as with a falling-film evaporator (K-4). The Navy has experience in designing and operating the Y-1 all electric vapor compression distilling unit

in early submarines (N-7). Similar to the vapor compressor evaporator is the vacuum degasifier. Producers of high purity water achieve low oxygen and CO_2 concentrations with the use of vacuum degasification (D-1). Reference M-7 also discusses the use of a vacuum degasifier in reverse osmosis (RO) high purity water production in the pharmaceutical industry to eliminate microbial contamination: it concludes that degasifiers are more economical at removing CO_2 than the previously used basic anion exchange.

Fig. D-2 shows a typical conventional vapor compression or vacuum degasifier (heating the seawater is an option, but not for this application, as noted earlier). The energy input for the seawater pump to pump 10,000 kg/sec of seawater at 15 ^{0}C (59 ^{0}F) with a pressure differential of 100,000 Pa (14.5 psia ~ one atmosphere) is equivalent to 0.27 kWhr/kg (418 Btu/lbm) of CO_2. The vapor, containing air, CO_2, and steam at 1380 Pa (0.2 psia) is compressed to 3450 Pa (0.5 psia) which has an associated saturation temperature of 26^{0}C (80 ^{0}F). The pressure of 3450 Pa (0.5 psia) was chosen to ensure a sufficient temperature differential such that the water vapor will be condensed in the heat exchanger. A nominal temperature differential of 10 ^{0}C (18 ^{0}F) was assumed. The work required for adiabatic compression of CO_2 is given by:

$$kW = \frac{k}{k-1}\left(\frac{W \times R \times T_i}{1000}\right)\left(\frac{P_2}{P_1}^{\frac{k-1}{k}} - 1\right) \qquad \text{(D-1)}$$

where:

k = 1.3 for CO_2
R = 189 J/kg^{0}K for CO_2
T_i = 285 ^{0}K for CO_2
P_2 = 3450 Pa for CO_2
P_1 = 1380 Pa for CO_2
W = 1 kg/sec for CO_2

This results in a power requirement of 0.015 kWhr/kg (23.6 Btu/lbm) of CO_2. Similarly, the pumping power to compress air can be calculated, knowing that k_{air} equals 1.4 and R_{air} equals 287 J/kg^{0}K. The power requirement is calculated to be 0.02 kWhr/kg (31 Btu/lbm) of air. However, the molar ratio of air to CO_2 in saturated seawater is approximately 0.33, and therefore the work to compress it is small and will be neglected (assuming a high extraction efficiency for CO_2).

Using steam tables, isentropic compression of the water vapor (steam) from 1380 Pa (0.2 psia) to 3450 Pa (0.5 psia) is estimated to require 0.042 kWhr/kg (65 Btu/lbm) of steam. The mass ratio of steam to CO_2 is unknown; however assuming various mass ratios, a predicted energy requirement can be determined. The results are shown in Table D.1. A value of 10 kg of steam for every 1 kg of CO_2 will be assumed, resulting in 0.42 kWhr/kg of CO_2 to compress the water vapor.

Limited research exists on the actual ratio of steam to CO_2 gas in the degasifier vapor; however, work performed by the National Renewable Energy Laboratory (NREL) in conjunction with the Open Cycle Ocean Thermal Energy Conversion (OC-OTEC) system offers some guidance. They report the ratio of non-condensable gases in seawater to steam in the condenser eductor effluent is generally 40 % to 70 % (2.5 to 1.4 steam to gas ratio), depending on operation conditions (Z-1). Typically, the uncondensed steam is about 50 % (2.0 steam to gas ratio) of the exhausted gas (Z-2). Similarly, using design data for a 50 m^3/min (13,125 gpm) seawater vacuum deaeration system for an offshore seawater injection platform, the ratio of the water vapor removal rate (steam) to removal rate of non-condensable gases ranges from 0.4 to 1.0 (H-11). Although the removal rate

of CO_2 is not provided, assuming the same percentage of CO_2 in the total non-condensable gases (CO_2 and O_2) reported for the influent (7.5 ppm O_2 and 2.0 ppm CO_2), results in a ratio of steam to CO_2 of 2 to 4. Therefore, considering the limited (and vague) data, the assumption of 10 kg of steam to 1 kg of CO_2 may be a reasonable, and perhaps conservative assumption determining the energy requirement to extract CO_2 from seawater.

Table D.1
Estimated Energy Requirement to Compress Steam

kg of steam/kg of CO_2	kWhr/kg of CO_2
1	0.042
10	0.42
100	4.2
1,000	42

Note: All components are assumed 100 % efficient.

The energy requirement to compress CO_2 from 3450 Pa (0.5 psia) to atmospheric pressure is calculated to be 0.08 kWhr/kg (120 Btu/lbm) of CO_2. Similarly the condensate must be pumped to 1 atmosphere; however the energy input is a small fraction of the energy required to pump the seawater feed. Assuming 10 kg of steam for every 1 kg of CO_2, results in a pump work that is only 0.1 % of the seawater pump work. The total energy requirement is therefore 0.79 kWhr/kg (1130 Btu/lbm) of CO_2 and is shown itemized in Table D.2.

Table D.2
Energy Requirements for CO_2 Removal from Seawater with Vacuum Degassing

	kWhr/kg of CO_2
Seawater Pumping	0.27
CO_2 Compression to 3450 Pa	0.015
Steam Compression to 3450 Pa (assumes 10 kg of steam per 1 kg of CO_2)	0.42
CO_2 Compression to atmospheric pressure	0.08
Total	**0.785**

Note: All components are assumed 100 % efficient.

D.3 Modified Vapor Compression Tower

A proposed modified vapor compression or vacuum degasifier tower is shown in Fig D.3. The major difference between this process and that described in section D.2 is the provision of a 10 m (33 ft) hydraulic head of seawater on the pump suction. Therefore, the seawater pump only must overcome a limited differential pressure of 10,300 Pa (1.5 psia) to account for assumed pressure losses within the system. This results in an energy requirement of 0.028 kWhr/kg (43 Btu/lbm) of CO_2, which is substantially lower than the previous process, which pumped against an atmosphere of pressure. Other pumping and compression requirements remain the same. The energy requirements for this process total 0.54 kWhr/kg (835 Btu/lbm) of CO_2 and are shown itemized in Table D.3.

Table D.3
Energy Requirements for CO_2 Removal from Seawater with Modified Vacuum Degassing

	kWhr/kg of CO_2
Seawater Pumping	0.028
CO_2 Compression to 3450 Pa	0.015
Steam Compression to 3450 Pa (assumes 10 kg of steam per 1 kg of CO_2)	0.42
CO_2 Compression to atmospheric pressure	0.08
Total	**0.543**

Note: All components are assumed to be 100 % efficient.

The process of vacuum degassing for CO_2 extraction from seawater should be optimized for CO_2 production. The processes mentioned above have all been optimized either for the production of fresh water (desalination) or elimination of detrimental non-condensable gases in high purity water. Therefore it may be that with further study the vapor degassing process can achieve a lower energy requirement than 0.54 kWhr/kg of CO_2. Additionally, it was assumed that 100 % of the total CO_2 in seawater was able to be extracted. Equation D-2 shows the forms and relevant amounts of CO_2 in seawater at equilibrium conditions.

$$\underset{1\ \%}{CO_{2(g)} + H_2O_{(l)}} \Leftrightarrow \underset{90\ \%}{H^+ + HCO_3^-} \Leftrightarrow \underset{9\ \%}{2H^+ + CO_3^{-2}} \qquad \text{(D-2)}$$

(% in seawater)

CO_2 extraction from seawater experiments must be conducted to determine the actual CO_2 extraction percentage and fully understand the kinetics of such reactions. However, if, say, only 15 % of the CO_2 can be extracted, then the energy requirements for this specific process will be approximately the same as that for H_2 production, and the overall process would therefore be too energy intensive.

D.4 Volume of Water to Produce Carbon Dioxide and Hydrogen

It is readily obvious that a large flow rate of seawater is necessary to provide the CO_2 for the synthetic fuel plant. A production rate of 1 barrel of $(CH_2)_n$ per hour, including the conversion inefficiencies, results in approximately 8600 moles of $(CH_2)_n$ per hour. Knowing that on a stoichiometric basis it takes 1 mole of CO_2 to produce 1 mole of $(CH_2)_n$ results in about 380 kg/hr of CO_2. Therefore, assuming 100 ppm CO_2 in seawater at a temperature of 15°C (59 °F) results in a seawater flow rate of 1.0 m^3/sec (980,000 gph) for every barrel of $(CH_2)_n$ per hour. However, to supply a CVN battle group 8,200 barrels of fuel per day are required, which requires about 350 m^3/sec (8 billion gallons of seawater per day). For comparison, the offshore seawater injection vacuum deaeration system (H-11) mentioned previously, has a rated seawater flow rate of 0.8 m^3/sec (18.6 million gallons per day) or about 0.2 % of that required for the "nuclear fleet oiler". For a 350 m^3/sec (8 billion gpd) seawater flow rate, an intake flow area of 11.1 m^2 (120 ft^2) is required, assuming a flow velocity of 10 m/s (33 ft/s). Although this is a large flow area, it is not prohibitive, especially if multiple (~10) vacuum deaeration towers are employed. Again for comparison, 3600 MW_{th} from a 25 % thermal efficient steam plant are required for the "nuclear fleet oiler". The required seawater flow rate through its main condensers

would be 43 m^3/sec (982 billion gpd) or about 1/8 of the seawater flow rate required for CO_2 production.

Similarly, the value of pure water required for electrolysis can be calculated knowing that 1 mole of water produces 1 mole of H_2. However it requires 3 moles of H_2 for every mole of $(CH_2)_n$. Therefore a production rate of 1 barrel of $(CH_2)_n$ per hour, including the conversion inefficiencies, results in the need for approximately 454 kg/hr (120 gph) of pure water (1.2 kg steam per kg CO_2). This is 0.01 % of the seawater flow rate, and could be produced entirely from the vacuum degasifier system (note we assumed 10 kg steam per kg CO_2 in that unit). This also confirms that the salt content of the system effluent is virtually indistinguishable from that of the feedwater. Operation of the vacuum degasifier is therefore well outside the normal envelope for distillation plants which typically result in a 50 % brine discharge (K-4).

D.5 Other Processes

Reference S-8 proposed a method using a stripping tower with steam and hydrogen at 1 atmosphere of pressure to strip CO_2 from seawater. Although this process is different than that employed in a vacuum degasifier, the quoted energy requirements are about the same. The reported energy requirement was 0.353 $kWhr_e$/lb of CH_3OH, which converts to 0.57 $kWhr_e$/kg of CO_2. However this process heats the seawater to 100 ^{0}C (212 ^{0}F), which was showed earlier to be too energy intensive for this application. In reference S-8 it was estimated that more than 75 % of the bicarbonates and carbonates can be stripped out along with the dissolved CO_2 at 100 ^{0}C. Furthermore, this process uses H_2 as an inert carrier gas to strip out CO_2. It would appear that H_2 stripping is not advisable

for this application since it was shown that H_2 production is the most energy intensive process involved, and any losses of this valuable commodity would be quite costly.

Some aspects of large scale seawater desalting technology may also be relevant to the current application. For example, deaerator - decarbonator units have been tested which reduce O_2 to <100 ppb and CO_2 to <6 ppm (P-11). However most such plants add acid to help liberate the CO_2, and may also add other chemicals to reduce foaming, scaling and biofouling. None of these options are suitable in the present initiative because of the large volumes of water processed, and also because of environmental concerns. Some of these systems do, however, employ large vapor compressors - a key component in the proposed synfuels plant. Again, however, desalting plants would usually employ feed preheat - an option which is not economic in the present instance.

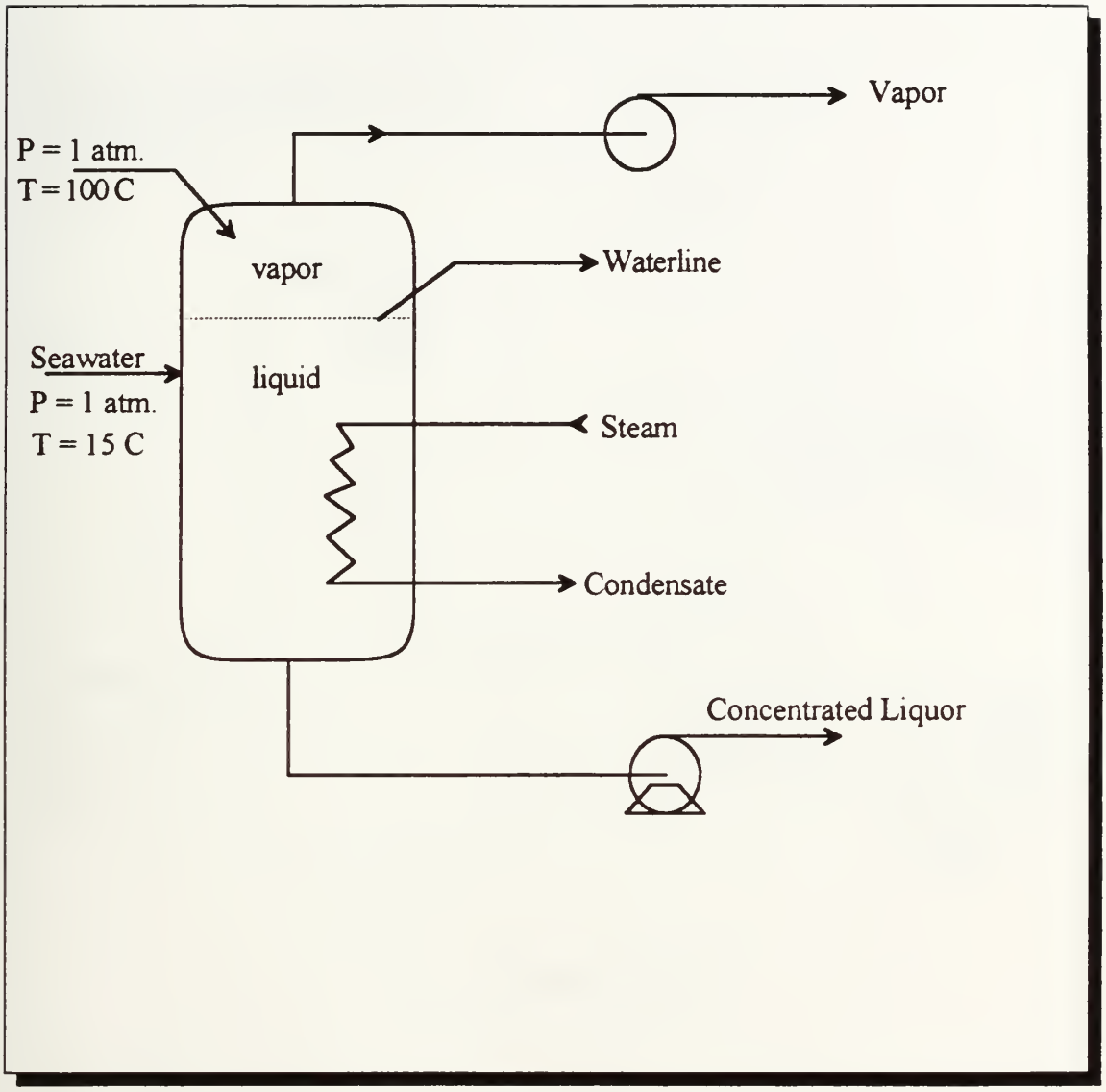

Figure D.1
Single Effect Evaporator

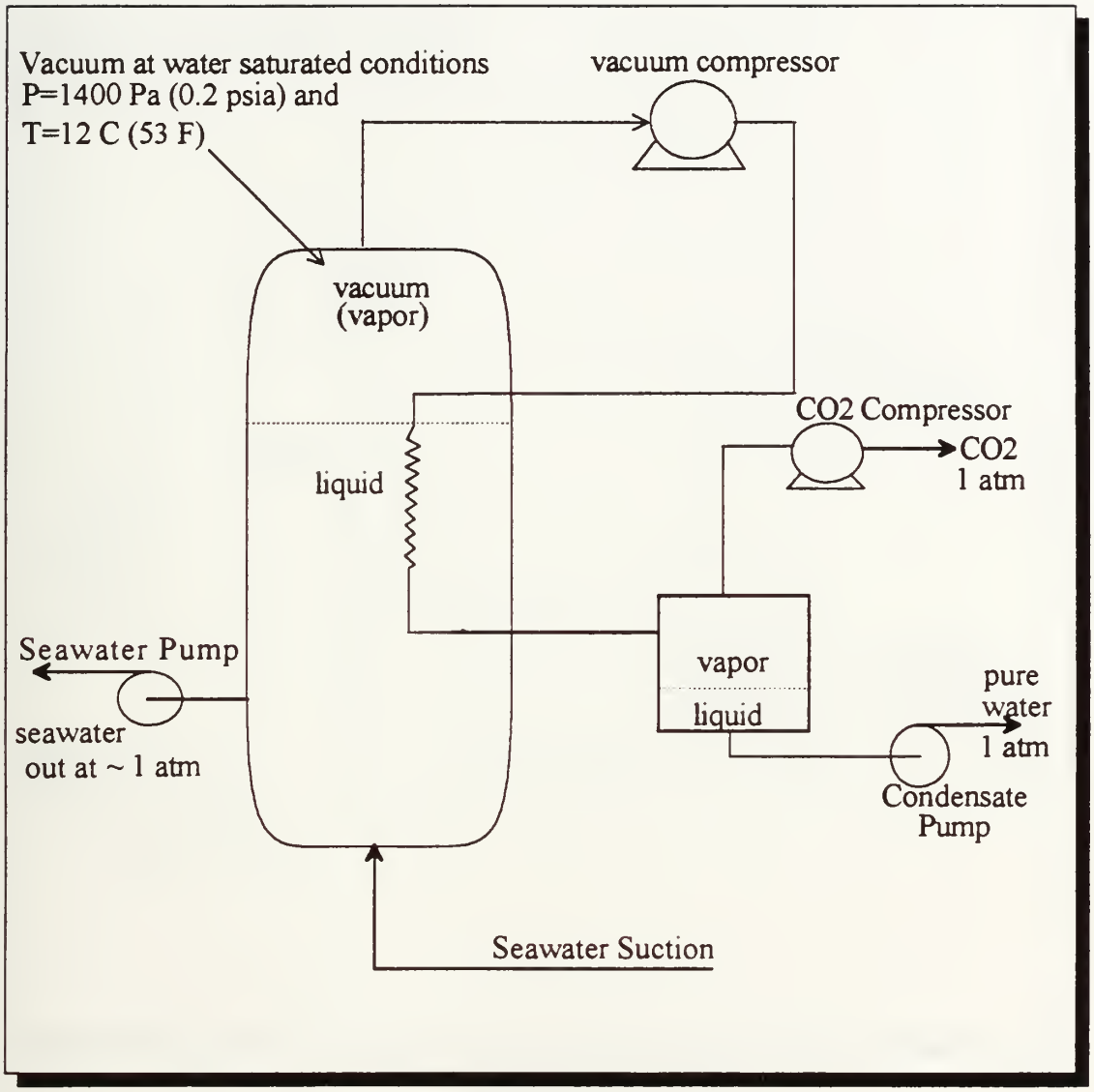

Figure D.2
Conventional Vapor Compression Process

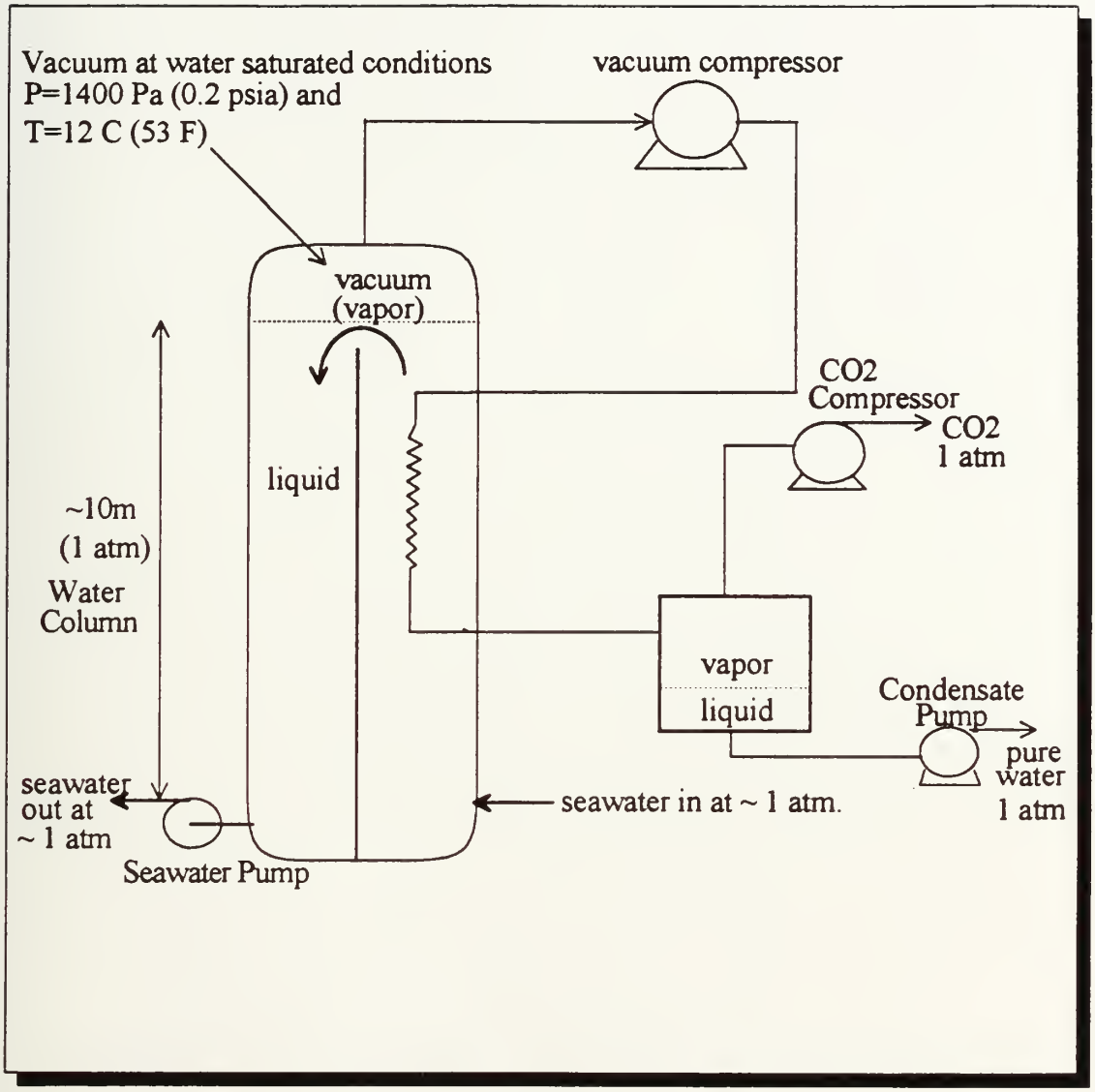

Figure D.3
Modified Vapor Compression Process

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